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### References


Lane, B. H., 1935. Suggestions to authors of papers submitted for publication by the United States Geological Survey: U. S. Geol. Survey, Washington, D. C. (For sale by Superintendent of Documents, Washington, D. C., 25¢.)

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American Journal of Science

*FEBRUARY 1951*

# THE SYSTEM $K_2O$-MgO-$SiO_2$[1]

## PART 1

EDWIN WOODS ROEDDER

ABSTRACT. The phase diagram of the more geologically significant portions of the condensed system has been determined by the quenching technique. Four new ternary compounds were found and their thermal relationships determined. Their compositions are $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and $K_2O \cdot MgO \cdot SiO_2$(?). The first of these may occur naturally but has not been reported, possibly because of its optical similarity to quartz. The second and third appear to be isomorphous with leucite and kalsilite, respectively, and the last is of comparatively little geologic interest. Thermal, optical, and X-ray data are given for these compounds, and composition and temperature have been determined for 28 of the invariant points occurring in the system. Experimental technique, crystallization behavior, and geological application are discussed briefly.

### INTRODUCTION

THE immediate purpose of this study was to aid the investigation of the four-component system $K_2O$-MgO-$Al_2O_3$-$SiO_2$ by Dr. J. F. Schairer,[2] which was studied because of its bearing on the stability relationships of the magnesian minerals forsterite, clinoenstatite, and cordierite, and the potash-alumina-silica minerals leucite, potash feldspar, and quartz. Four ternary systems limit the quaternary system $K_2O$-MgO-$Al_2O_3$-$SiO_2$. One of these, $K_2O$-MgO-$Al_2O_3$, has not been investigated because of the lack of direct geologic interest; two others, MgO-$Al_2O_3$-$SiO_2$ (Rankin and Merwin, 1918) and $K_2O$-$Al_2O_3$-$SiO_2$ (Schairer and Bowen, 1947a), have been studied previously; the fourth, $K_2O$-MgO-$SiO_2$, is the subject of this report. Although there is no naturally occurring mineral known consisting of $K_2O$, MgO, and $SiO_2$, during the course of the work several new ternary compounds of interest to petrology and mineralogy were found and are reported here.

[1] A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University, 1950.

[2] Preliminary report in abstracts of papers presented at the meeting of the Geological Society of America in New York, 1948.

Potash, magnesia, and silica are among the seven most abundant constituents of igneous rocks, and Washington (1915) has shown a direct relationship between the amounts of potash and magnesia in certain rocks. The system is of interest also in the broader problem of the chemistry of silicate formation and stability. Only that portion of the condensed system higher in silica than the join $K_2O \cdot SiO_2$-MgO was studied.

In addition, the work was part of a long term project being carried on at the Geophysical Laboratory on the stability relations of the rock-forming dark micas—the biotites (Adams, 1947). As biotites are essentially hydrous, potash-magnesia-alumina silicates with a partial substitution of $Fe^{++}$ for $Mg^{++}$, their compositions lie within the six-component system $K_2O$-MgO-FeO-$Al_2O_3$-$SiO_2$-$H_2O$. Since the presence of water and iron oxide causes considerable experimental difficulty, the most reasonable approach was a study of the system $K_2O$-MgO-$Al_2O_3$-$SiO_2$. A knowledge of the limiting system $K_2O$-MgO-$SiO_2$ is essential to an understanding of this quaternary system. The only previous work on the system $K_2O$-MgO-$SiO_2$ involved the addition of water as the fourth component to a small range of compositions with the formation of hydrated mica-like clay minerals (Noll, 1944). Another possible application of the system $K_2O$-MgO-$SiO_2$ is in the further study of the system MgO-$SiO_2$-$H_2O$ (Bowen and Tuttle, 1949) where the addition of $K_2O$ may aid the formation of a liquid phase (Adams, 1947).

This work was done at the Geophysical Laboratory of the Carnegie Institution of Washington on a one-year fellowship. The writer wishes to thank the Director of the Laboratory, Dr. L. H. Adams, for this opportunity, and Dr. J. F. Schairer, under whose direction the work was done, for his aid and encouragement. The writer is indebted also to the other members of the Laboratory for many helpful suggestions, and particularly to Drs. Schairer, Morey, and Yoder for a critical reading of the manuscript; however, the writer alone is responsible for any errors which may occur. He also expresses his appreciation for the cooperation, assistance, and advice of the members of the staff of the Geology Department of Columbia University, particularly to Professor C. H. Behre, Jr., who initiated the original discussions leading to the au-

thor's connection with the Geophysical Laboratory; to Professor Paul F. Kerr for his cooperation in making this arrangement possible; and to Professor Ralph J. Holmes for advice on X-ray diffraction techniques.

## EXPERIMENTAL PROCEDURE

*Raw Materials.*—The starting materials for most of the compositions were $KHCO_3$, quartz, and MgO. The $KHCO_3$ was of reagent grade,[3] and was prepared by crushing to a powder and drying over KOH. The quartz used was the regular Geophysical Laboratory supply of Lake Toxaway quartz, crushed and leached with HCl. Analysis by J. W. Greig gave a residue of 0.04 per cent (using 5 grams) on evaporation with HF and $H_2SO_4$. It was prepared for weighing by heating for two or more hours at 1500° C.[4] This heating serves to eliminate liquid inclusions and converts the quartz to cristobalite, facilitating subsequent grinding in an agate mortar. In a few special batches Mallinckrodt "Special Bulky" silicic acid was used because of its fine grain size,[5] but in these cases a water analysis had to be made simultaneously because of its large and variable amount (15.5 per cent). The MgO used was reagent grade,[6] although analysis by J. F. Schairer showed 0.2 per

[3] J. T. Baker Chemical Co., Lot no. 12733 analysis:

| | per cent |
|---|---|
| Cl | 0.003 |
| $PO_4$ | 0.001 |
| $NH_3$ | 0.000 |
| Fe | 0.000 |
| $SO_4$ | 0.001 |
| Heavy metals (as Pb) | 0.000 |
| Ca, Mg, and $NH_4OH$ ppt. | 0.00 |

[4] All temperatures are in degrees Centigrade.

[5] The powder has a bulk density of only 0.11 grams per cc.

[6] J. T. Baker Chemical Co., Lot no. 82735 analysis:

| | per cent |
|---|---|
| Insol. in HCl | 0.02 |
| Loss on ign | 2.5 (10.35 E. R.) |
| Soluble in $H_2O$ | 0.4 |
| Heavy metals (as Pb) | 0.0035 |
| $NH_4OH$ ppt. | 0.02 |
| $(NH_4)_2S$ metals (as Fe) | 0.008 |
| Sulfate and sulfite | 0.005 |
| $SiO_2$ | 0.01 |
| Cl | 0.008 |
| $NO_3$ | 0.005 |
| Ca | 0.05 (<0.2 J. F. S.) |
| Ba | 0.005 |

cent total alkalies. It was prepared for weighing by heating to 1500° for one hour. This minimizes water adsorption, but corrections still had to be applied to each portion weighed, as determined by individual weight-loss measurements upon ignition of each portion weighed.

*Preparation of Potassium Silicates.*—In almost every case the $KHCO_3$ was first converted to a pure, completely crystalline potassium silicate compound ($K_2O \cdot 4SiO_2$, $K_2O \cdot 2SiO_2$, or $K_2O \cdot SiO_2$) before using in order to minimize volatilization of $K_2O$ during the preparation of the various compositions. A glass of the composition of the desired potassium silicate compound is first made by mixing together on low-ash filter paper the stoichiometric amounts of $KHCO_3$ and $SiO_2$ to give 20 grams of the silicate. The mixture and the paper are put into a 40 cc. platinum crucible, carefully heated up to 1000° over a predetermined 48-hour heating schedule to minimize foaming and volatilization of $K_2O$ (Kracek, 1932, p. 2529), and finally heating for two hours at 1300°. When cool it is weighed; any loss in weight in excess of the $CO_2$ and $H_2O$ given off by the $KHCO_3$ is attributable only to volatilization of $K_2O$ and must be corrected for by the addition of the calculated amount $KHCO_3$.[7] Furthermore, the batch is far from homogeneous at this stage and must be carefully removed from the crucible, crushed, replaced, and remelted again for two hours at 1300°, the process being repeated until a completely homogeneous glass is obtained. The extremely hygroscopic nature of this glass and the persistence of small amounts of $CO_2$ make is necessary to crystallize it, this being done by holding it at appropriate lower temperatures with occasional crushings until it remains a completely crystalline powder at the temperature of the furnace. As long as uncrystallized glass is present the powder will sinter together in the furnace. This crystallization is completed in 3 to 4 days,[8] after which the

[7] The amount of this volatilization of $K_2O$ is small—usually less than 10-20 mg. in a 20 gm. batch—but sufficiently variable due to irregularities in the process that it must be corrected for in each batch separately. After this first fusion at 1300° further volatilization is found to be insignificant, and the volatility of silica at these temperatures is practically nil (see Sosman, 1927, p. 109). In those cases where the metasilicate, $K_2O \cdot SiO_2$, was made up, failure to eliminate all of the $CO_2$ caused troubles which will be considered beyond under "Alkali Losses."

[8] "Seeding" with previously obtained crystals has to be resorted to in the case of $K_2O \cdot 4SiO_2$ because of its sluggish crystallization.

crystalline powder may be kept over KOH with little gain in weight except in the case of $K_2O \cdot SiO_2$.

*Preparation of Batches.*—All except the high alkali compositions were determined entirely by synthesis. The calculated amounts of potassium silicate, magnesia,[9] and silica were weighed out to make the individual compositions listed in table 1. Ten grams was a convenient amount to make and should be less affected by systematic errors. Each batch was carefully mixed on low-ash filter paper and heated to 1300-1500° in a 15 cc. platinum crucible for one or more hours,[10] depending upon the viscosity of the liquid, then quenched, crushed,[11] replaced in the same crucible, and fused again. This process was repeated until a homogeneous glass was obtained. The homogeneity was checked by microscopical examination of the crushed glass when immersed in an index oil exactly matching the glass, making use of the more rapid change of the index of refraction of the oil with change in temperature to obtain a perfect match. Extremely small local variations in the composition of the glass result in index variations which are rather prominent by this method. Viscous batches may take five or even more such fusions alternating with crushings before becoming homogeneous.[12] As has been emphasized else-

[9] The small amount (0.05-0.10 per cent) of water taken up by the MgO during storage over KOH (following the 1500° ignition) was corrected for by weighing out the magnesia first into the crucible, igniting at 1300° for 15 minutes, reweighing and correcting for the loss in weight before adding the other components.

[10] Weight loss determinations on a number of such batches (using a smooth plate cut from a corundum crystal as a plaque) showed practically neglible volatilization of alkalies, as changes in weight were within the limits set by the vaporization and condensation of platinum in the furnace at such temperatures. In the high alkali portion of the system weight losses were sizable (see "Alkali Losses" beyond).

[11] The laborious process of fine grinding of many samples is made considerably easier through the use of a Plattner-type hardened steel "diamond" mortar with the crushing end of the pestle of smaller diameter than the main pestle shaft and eccentric to it. The use of a steel mortar is recommended in place of other materials because contamination of the sample can be kept to a minimum through magnetic separation after each grinding. It has been shown (Sandell, 1947) that, without magnetic separation, grinding of quartz in a Plattner-type mortar yields 0.02 to 0.03 per cent Fe in the ground material.

[12] The higher alkali glasses cannot be made perfectly homogeneous by this method as small variations in index persist indefinitely, presumably due to volatilization of alkali from the surface. The later crystallization of these glasses, however, forming crystals with individual compositions different from that of the glass, represents a far greater degree of "inhomogeneity" than occurs in the glass.

where, this homogenization is an important and essential step if true equilibrium is to be obtained in the subsequent quenching experiments with the material.

*Crystallization of the Batches.*—All compositions were precrystallized partially or completely before quench runs were made.[13] To do this a portion of the homogeneous glass obtained above was held at temperatures which were 50 to 100°[14] below the approximated liquidus (as predicted by experience and extrapolation from nearby points). The viscosity of the more viscous glasses increases rapidly with decrease in temperature, hence the crystallization velocity is so small as to be experimentally impractical if crystallization is attempted at much more than 100° below the actual liquidus, and, of course, no crystallization can occur if held above the liquidus temperature. Even under optimum conditions (correct temperature, frequent crushings, etc.) batches in the vicinity of the two lowest ternary eutectics did not begin to show visible crystals (1-2 microns in length) within the first month of crystallization. Such batches could not be completely crystallized in the time available for these studies, but many of the others could be, and these completely crystalline preparations were useful in determining eutectic temperatures. The viscosities of the glasses in a few cases were found to be so high that the powdered glass would not flow together to a coherent mass even when held for 24 hours at temperatures near the liquidus. Elsewhere in the system the viscosities were lower and liquidus temperatures were higher, so crystallization was usually initiated within a few days or even within a few seconds (in the very high temperature, low silica melts). Microscopical examination at frequent intervals during the crystallization provides a very rough but useful indication of the phases and temperatures to be expected during the quenching experiments. Wherever possible coarse crystallization was avoided

[13] In most silicate studies this is essential because of the sluggishness of crystallization compared with melting. In some cases it was found that compositions which required months at optimum temperatures to form the first visible crystal nuclei and weeks more, with frequent crushings, to convert even a small percentage of the glass to crystals, would attain equilibrium in less than a week in the quenching runs, where equilibrium is approached by melting rather than by crystallisation.

[14] H. R. Swift (1947) found that 40-100° gave the highest rate of crystal growth for a number of silicate compounds but that there was wide variation. See also the discussion of crystallization velocity in Tammann (1925).

because of the long time necessary to attain equilibrium between crystals and liquid during the quenching experiments with such material. A few of the more viscous melts with very low liquidus temperatures had to be subjected to "hydrothermal" conditions[15] in order to induce crystallization, but in these cases subsequent "dry" crystallization was usually possible (on another portion of the glass) after the correct temperature range had been determined on the "hydrothermally" formed crystals.

*Quenching Technique.*—All of the equilibrium data was obtained by the quenching technique (Shepherd, Rankin, and Wright, 1909; Ferguson and Merwin, 1919; Faust, 1936; and Hill, Faust, and Reynolds, 1944). A charge of about 10 mg. of the crystalline material in a small 0.01 mm. platinum-foil envelope[16] is suspended in the hottest portion of the furnace (region of minimum thermal gradients), with a thermocouple junction about 1 mm. to the side of the center of the envelope, for a length of time sufficient to attain equilibrium

[15] The method used involved sealing two cylindrical loosely-covered, platinum-foil capsules into a fused silica tube. One capsule contained approximately 0.2 gm. of the powdered glass to be crystallized and the other about the same amount of ground obsidian. The obsidian used was that from Mono Craters, California, containing approximately 0.07 per cent F, 0.13 per cent Cl, 0.2 per cent $H_2O^+$, an unknown amount of $H_2S$, and with $SiO_2$ and $Al_2O_3$ 76 and 12 per cent respectively (see Shepherd, 1938). A sample of the ground obsidian was fused and showed a 0.41 per cent weight loss when ignited over a Meker burner.

The whole tube was then put into the furnace at about 100° below the estimated liquidus of the glass to be crystallized. The heat drives some of the volatile "mineralizers" out of the obsidian and into the atmosphere of the tube, from which a portion is absorbed by the glass sample. Although the partition of these volatiles between the obsidian, the tube atmosphere, and the glass sample is not known, the glass can hardly have more than one-third of the total amount present, and may possibly have much less, but this small amount of "volatiles" dissolved in the glass is adequate to induce crystallization in extremely viscous glasses in 24 hours, where holding for one month at the correct temperature in the "dry" condition (*i.e.*, with only the partial pressure of water naturally occurring in the air in the furnace) caused no crystallization.

[16] To make these envelopes a piece of foil approximately 10 x 16 mm. is folded so that the 10 mm. edges are together. The 8 mm. sides are then folded back over themselves twice, taking about 1 mm. each time. The resultant 6 x 8 mm. envelope is spread open at the top, the charge is inserted, and the top is then folded down. A pinhole through this top fold permits hanging. If the folds are pressed tightly, they will not leak, except in the case of high-alkali compositions where a double envelope is needed.

and then dropped out of the furnace into cold mercury by suddenly melting a thin (0.2 mm.), supporting, platinum wire by an electric current. The "quenched" foil envelope is torn apart and the crushed sample examined with standard petrographic immersion methods (and X-ray where necessary and possible) to determine what crystalline phases were present at the temperature of the furnace, any liquid present having quenched to a glass. In a few cases, particularly at high temperatures and where quenching was not as rapid as desired, feathery crystals formed around each of the euhedral crystals present in the glass, or around other nuclei such as the thin platinum crystals that form on the surface of the melt from furnace vapors. Because the amount of such crystallization varied directly with the quenching time, the feathery crystals obviously formed on quenching and could be ignored.

One minor change in the usual technique permitted the heating of a larger number of different quench charges simultaneously within the same furnace.[17] Previously porcelain rings were used as separators between the platinum envelopes of such charges to prevent the welding together of the platinum surfaces. The substitution of slips of ordinary white glazed paper for these porcelain rings was found satisfactory, the ash from the paper being sufficient to keep the platinum surfaces from touching at temperatures below 1040°. Above this temperature fusion of the paper ash makes it necessary to substitute filter paper slips, dipped in a thin suspension of MgO. With this procedure 10 runs could be made simultaneously whenever desired. Even with 10 envelopes, the resultant bundle is smaller than the former maximum bundle of 4 envelopes and 3 porcelain rings, and also more thermally conductive, resulting in smaller thermal gradients throughout the bundle and more rapid quenching.

*Determination of Equilibrium.*—The attainment of equilibrium in the quench runs was established by several criteria:

1. Absence of rounded or corroded crystals—this is not a reliable criterion either as positive or as negative evidence but is a useful indication.

[17] Whenever possible several different charges were run simultaneously to save furnace time. The bundle of charges was sufficiently small to be entirely within the region of negligible temperature variation, a cylindrical space approximately 1 x 1 cm. By this procedure differences between batches could be detected even though they were smaller than the accuracy of the calibration of the thermocouple.

2. Agreement of data with nearby points and with other data on the same point—this is particularly useful.

3. Duplication of results by starting with the same composition in a different physical state (*e.g.*, crystalline and glassy)—this is experimentally feasible only in the more easily crystallized batches.

4. Lack of further change when held at the same temperature for a longer time—this is the best criterion.

5. Uniformity of distribution of the phases—this is useful to detect inhomogeneity in the original sample.

None of these criteria is really adequate to detect differences between stable and metastable equilibrium when the change is sluggish as in the extension of the field of tridymite over that of quartz, and the fourth is of no value in the high alkali preparations where the composition is changing during the duration of the run. The third criterion was applied in many cases but only the data for the crystalline material are given in the following tables to save space. Initiation of crystallization was so sluggish in most cases that nuclei (traces of crystalline material) were added to all quench runs starting with glassy material. As with many silicate systems the determination of the appearance of a phase at equilibrium practically requires that that phase be present, at least in traces, in the starting material, whether it be mainly crystalline or glassy. For this reason compositions having complicated crystallization paths involving the formation and subsequent disappearance of several phases during the cooling history were crystallized by various methods on separate portions, so that starting material having all the necessary phases present to establish a given phase change was available for each such determination. Obvious cases of minor local inequilibrium such as failure of a crystal to react with liquid owing to its inclosure by another crystal have been ignored in the data tables. Approximately 1300 quenching runs were made at temperatures which were not immediately adjacent to the temperature of a phase change and hence are not listed in the tables of quenching data. These served, however, as confirmatory evidence to substantiate those runs made at the more critical temperatures. In those cases in the data tables where two runs establishing a phase change have been made for different lengths of time, confirmatory runs at nearby tempera-

tures during the course of the work had established the shorter length of time as adequate to obtain equilibrium.

*Temperature Measurement.*—Temperatures were determined with thermocouples of Pt against Pt 90 Rh 10 measured with a shielded, double White potentiometer and galvanometer system reading directly to microvolts. The annealed thermocouples (Roeser and Wensel, 1935) were calibrated as frequently as drifting necessitated.[18] The melting points of pure NaCl (800.4°), gold (1062.6°), diopside (1391.5°), and pseudowollastonite (1544°) were used to establish the temperature scale. The NaCl was prepared for use by two precipitations with concentrated HCl from a solution of high purity reagent grade NaCl, followed by washing, drying, grinding, and final drying at 100°. It had a negligible melting range. The gold was "proof gold," obtained from the U. S. Mint, and also had a negligible melting range. This was not true of the diopside and pseudowollastonite, which, though synthesized from the purest available chemicals, had appreciable melting ranges (about 30 and 10 microvolts respectively from the first visible liquid formation to the disappearance of the last crystal). For this reason the temperature of melting of the last trace of crystals was considered to be the melting point. These four melting points are thus the basis of all of the temperature measurements, the deviation of the thermocouple from standard reference tables being used for convenience in interpolation (Sosman, 1910).

Many of the possible sources of error in the correct measurement of temperatures are eliminated or minimized by performing the calibration runs in exactly the same manner as the quenching runs,[19] so that thermal gradients within the sample

[18] The drift between calibration runs is variable and only its order of magnitude is predictable. High alkali compositions and high temperatures considerably increase the rate of drift. A platinum quench envelope sticking to a thermocouple necessitates immediate recalibration. The use of iridium-free platinum throughout the apparatus aids a great deal in stabilizing the emf of the thermocouples. (See Day, Shepherd, and Wright, 1906, p. 286.)

[19] In the case of gold calibration, a tiny sliver of gold sheet is held in a thin porcelain tube 5 mm. long with asbestos plugs. This tube is then inserted in a platinum envelope similar to those used in the quenching runs. After the calibration run the sliver is examined; if the temperature was below the melting point of gold, the sliver will be unaffected; if above, it will have coalesced to a globule. The coalescence from a white powder to a clear mass indicated melting in the case of NaCl. The diopside and pseudowollastonite runs were examined microscopically for amounts of glass and crystals.

and thermocouple are identical in both cases. The effect of inhomogeneities in the thermocouple wire away from the junction itself and differences in the temperature of the thermocouple junction and the sample itself thus become relatively insignificant. All cold junctions were kept in melting ice.

The hottest portion of the furnace varies with temperature and time and hence must be located prior to the run by exploring the furnace tube with the thermocouple; the thermal gradients and sample size are such that no portion of the sample may vary more than a few tenths of a degree from that of the thermocouple junction, the method of calibration correcting for a portion of this. The details of furnace construction and regulation have been published previously (Adams, 1924; Roberts, 1925, 1941; and Faust, 1936). Furnace temperature control can be considered to be constant to $\pm 0.3°$ approximately for runs of a few hours duration and $\pm 0.5°$ approximately for longer runs. The temperature during runs of over six hours at temperatures of over 1400° was only constant to $\pm 1.0°$.[20]

The frequency of calibration of the thermocouples, and hence the accuracy to which any given temperature determination on the following pages was made, varied with the sensitivity of the phase change being measured,[21] the temperature, and the nature of the batch (change in composition during the run makes accurate temperature measurement superfluous in the high alkali batches). Relative temperature determinations made by running several samples simultaneously in the same furnace are, of course, far more accurate than absolute determinations. By this means small differences between batches could be detected although they were less than the absolute accuracy of the temperature measurements as determined by the calibration technique. The frequency and nature of the calibration and the spacing of the quenching runs were such that most of the liquidus determinations are accurate to $\pm 3°$. Whenever possible, more careful work was done in the vicinity

[20] This is due mainly to volatilization of platinum from the winding of the furnace and consequent change in its electrical resistance, since the furnace temperature control is based on the furnace winding being one "arm" of a balanced Wheatstone bridge.

[21] Theoretically phase changes should occur with an extremely small $\Delta T$, but in silicate systems of this type the rate of attainment of equilibrium makes such determinations experimentally impractical when $\Delta T$ approaches 1° or less, except for the more fluid batches and at the melting points of compounds.

of the invariant points, with the resultant accuracies as stated in table 5.

### LIMITING BINARY SYSTEMS

Three binary systems limit a ternary system. Two of the limiting binary systems, $MgO$-$SiO_2$ (Kanolt, 1913; Ruff, 1913; Bowen and Andersen, 1914; and Greig, 1927), and $K_2O$-$SiO_2$ (Niggli, 1913; Morey, 1914; Morey and Fenner, 1917; Kracek, Bowen, and Morey, 1929, 1937; Kracek, 1930a, 1932; Goranson and Kracek, 1932; and Kröger and Fingas, 1933), have been studied and the diagrams of these are reproduced in figures 1 and 2. All of the compositions prepared in this study were ternary mixtures, hence no new data was obtained on these limiting binaries. Extrapolation from the ternary data to the sidelines, however, is concordant with the data on these two binary systems. No data on the system $K_2O$-$MgO$ have been published, and since all compositions made

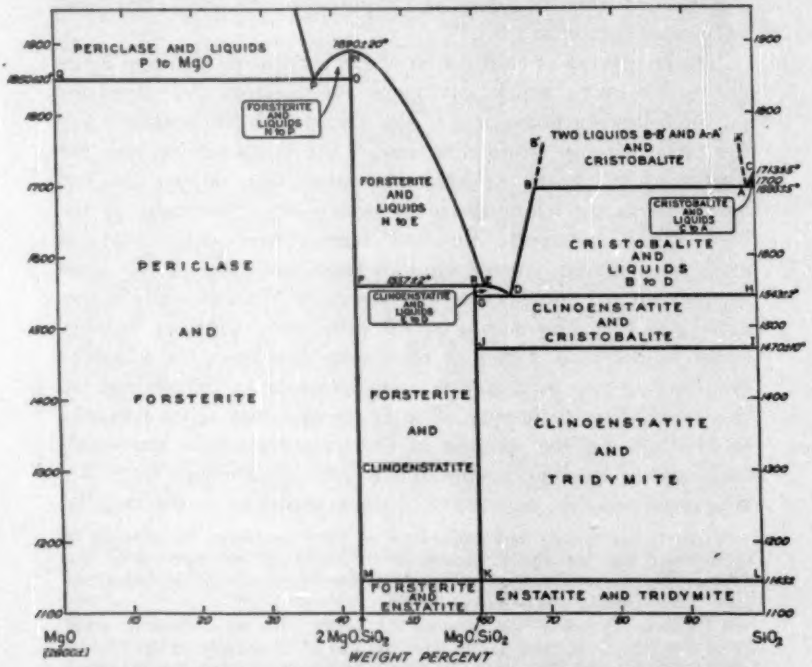


Fig. 1. Equilibrium diagram of the system $MgO$-$SiO_2$, after Bowen and Andersen (1914) as modified by Greig (1927).

in this investigation had over 30 per cent $SiO_2$ in them, nothing can be said here concerning it.

## EXPERIMENTAL RESULTS

*General Statement.*—The compositions by synthesis of the 133 mixtures studied are listed in table 1 and plotted on figure 3, along with the boundary curves (heavy, solid or dashed lines), fields (primary phase areas), and tie lines (light lines). Arrows on boundary curves indicate direction of falling temperature. Figure 4 is a plot of the isofracts and curves of

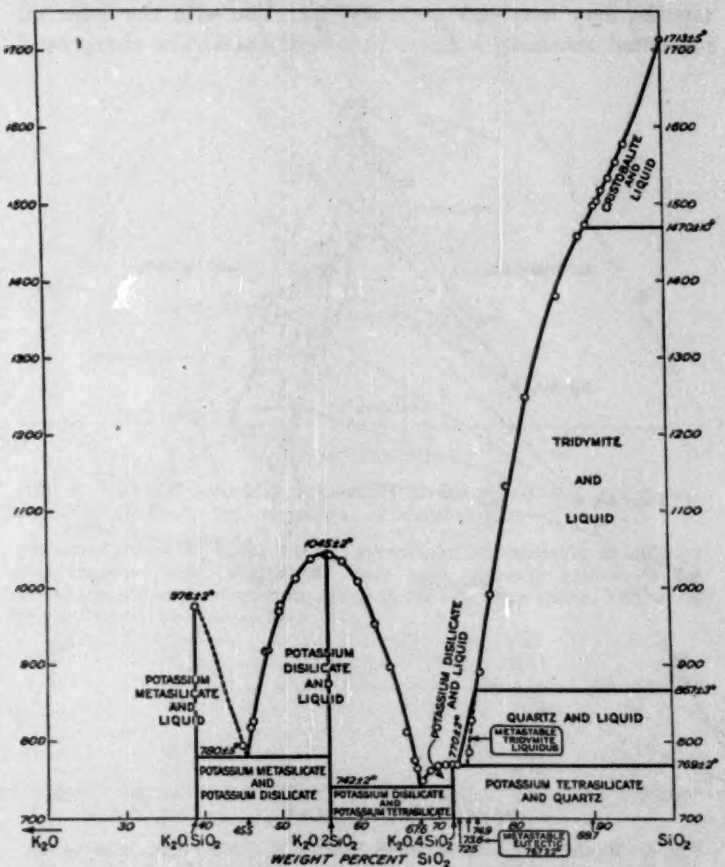


Fig. 2. Equilibrium diagram of a portion of the system $K_2O$-$SiO_2$, after Kracek, Bowen, and Morey (1937).

equal density for the various glasses obtained. The data for the indices of refraction are given in table 1. No great accuracy is claimed for these data; they were obtained by the immersion method, with white light, on the unannealed glasses quenched from temperatures above the liquidus. They were useful, however, in determining very roughly the composition of the liquid in some quench runs and as convenient checking details. Most of these indices are probably accurate to ± 0.003, although a few, particularly in the higher alkali portion where water adsorption and reaction with the index liquid causes trouble, may have less accuracy. Reaction with the index oil prevented obtaining a figure in several cases. The sharp bend

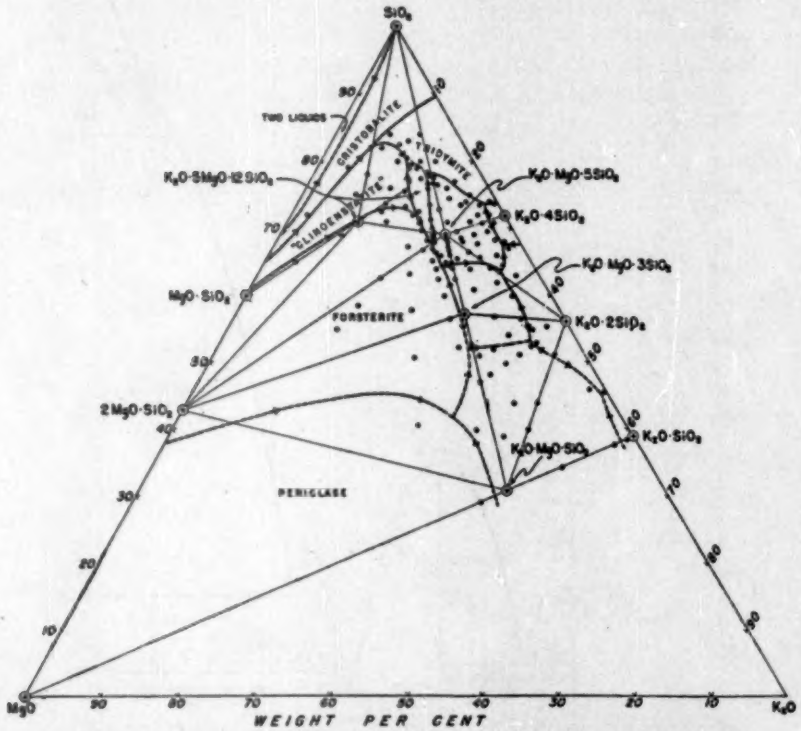


Fig. 3. Equilibrium diagram of the system $K_2O$-MgO-$SiO_2$, showing the compositions studied (plotted in weight per cent, by synthesis), compounds, boundary lines, and composition triangles (Alkemade lines). The tridymite field below 867° is metastable.

in the isofracts and in the curves of equal density[22] at the 1:1 $K_2O$:MgO ratio line of compounds is particularly inter-

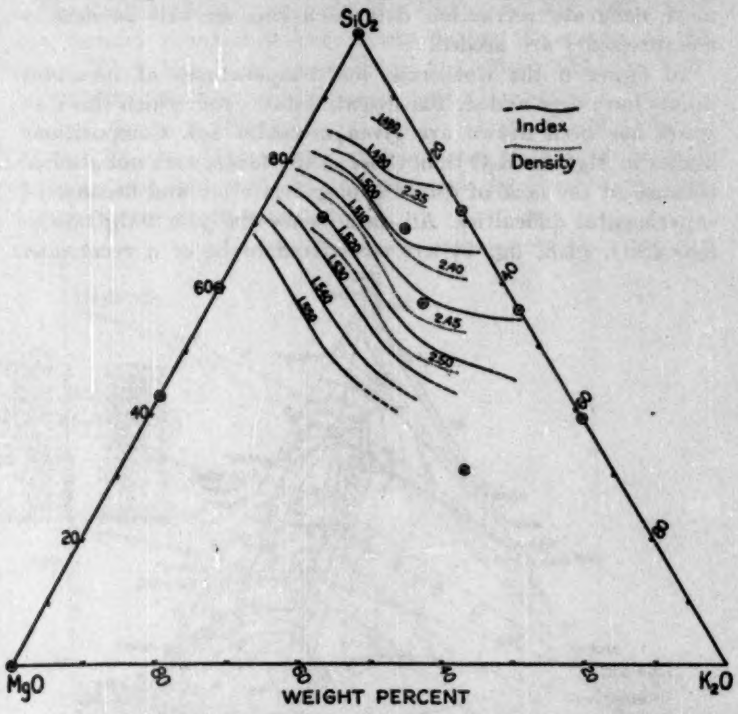


Fig. 4. Index of refraction and density of the glasses. See text for details. Circles indicate the composition of compounds.

[22] These curves of equal density are merely approximate as only 12 glass densities were determined; these data, although inaccurate for several reasons, were adequate to establish the curvature shown. The actual densities found were as follows:

| *Composition* | *d* |
|---|---|
| 2 | 2.44 |
| 8 | 2.48 |
| 10 | 2.54 |
| 11 | 2.40 |
| 17 | 2.50 |
| 25 | 2.38 |
| 28 | 2.41 |
| 32 | 2.38 |
| 58 | 2.44 |
| 72 | 2.39 |
| 75 | 2.36 |
| 80 | 2.34 |

esting in view of recent work on the effect of the molecular structure of glass on its properties (Lukesh, 1948), although more accurate refraction determinations as well as density measurements are needed.

In figure 5 the isotherms and temperatures of invariant points have been added. The essential data from which this diagram has been drawn are given in tables 1-5. Compositions higher in MgO or $K_2O$ than those in the tables were not studied because of the lack of direct geologic interest and because of experimental difficulties. All data below the join $2MgO \cdot SiO_2$-$K_2O \cdot 2SiO_2$ (*LE*, fig. 5) are considered to be of a reconnais-

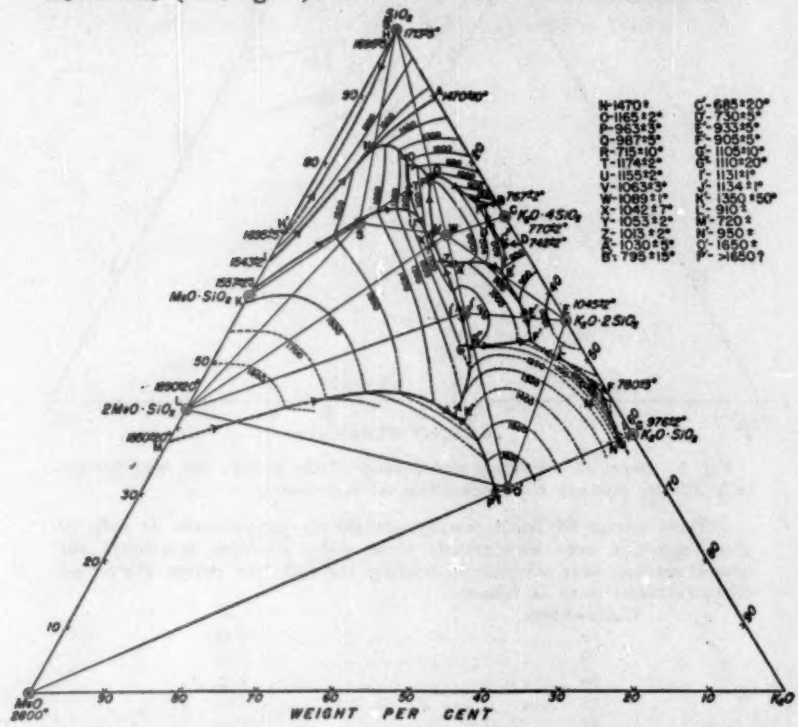


Fig. 5. Equilibrium diagram of the system $K_2O$-MgO-$SiO_2$, showing isotherms and invariant points. The tridymite field below 867° is metastable, hence binary eutectic point B and ternary eutectic point R are both metastable. For an enlarged plot of the sub-system Forsterite-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$ (triangle LWS') see figure 8. Data below a line between $2MgO \cdot SiO_2$ and $K_2O \cdot 2SiO_2$ (LE) are of a reconnaissance nature; see footnote 49.

sance nature, although they are fairly concordant among themselves. In addition to the compounds already known to occur in the limiting binary systems MgO-$SiO_2$ and $K_2O$-$SiO_2$, four new ternary compounds were found during the course of the work. They have the compositions $K_2O \cdot MgO \cdot SiO_2$(?), $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and $K_2O \cdot 5MgO \cdot 12SiO_2$. A portion of figure 5 (the triangle *LWS'*, $2MgO \cdot SiO_2$-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$) has been recalculated in terms of these three components and replotted on a larger scale in figure 8 to show courses of crystallization, etc.

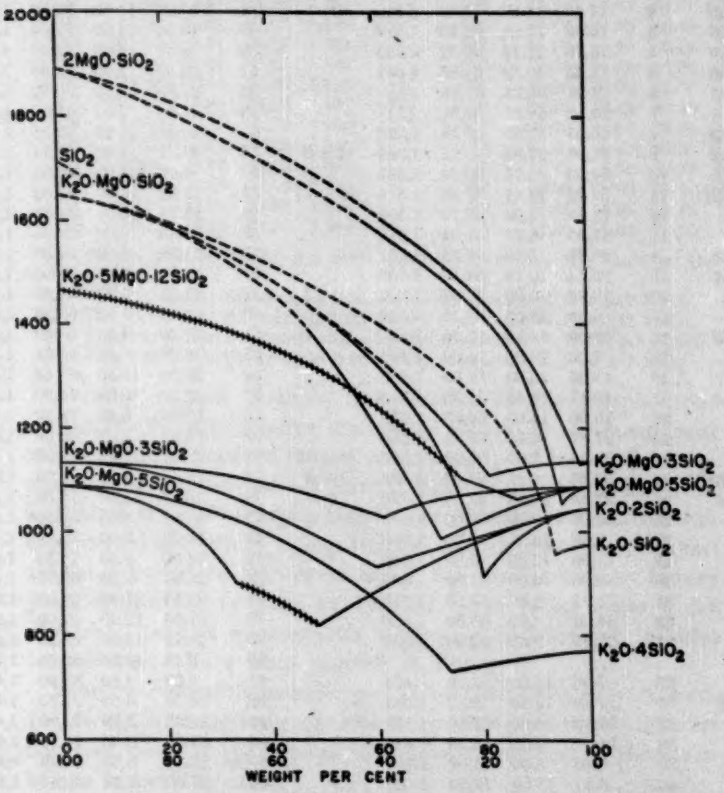


Fig. 6. Sections through the ternary system along the various binary sub-systems. The two cross-hatched lines indicate non-binary (ternary) equilibrium for those portions. Several of the binary systems that are almost wholly non-binary at liquidus temperatures have been omitted. Data taken from tables 1 to 3.

TABLE 1

## COMPOSITION OF THE PREPARATIONS STUDIED

**The percentages are weight per cent by synthesis (see text and table 7 for analysis of high alkali batches). The molecular weights used in the calculation were $K_2O$-94.20, MgO-40.32, and $SiO_2$-60.06. Mol ratio is the molecular ratio $K_2O$:MgO:$SiO_2$.**

| Mol Ratio | Prep. | Per Cent $K_2O$ | Per Cent MgO | Per Cent $SiO_2$ | n of Glass | Mol Ratio | Prep. | Per Cent $K_2O$ | Per Cent MgO | Per Cent $SiO_2$ | n of Glass |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1:1:6 | 1 | 19.03 | 8.15 | 72.82 | 1.499 | | 47 | 12.00 | 9.00 | 79.00 | 1.492 |
| 1:2:6 | 2 | 17.60 | 15.07 | 67.33 | 1.512 | | 48 | 16.00 | 12.00 | 72.00 | 1.499 |
| 1:3:6 | 3 | 16.36 | 21.01 | 62.63 | 1.528 | | 49 | 13.00 | 16.00 | 71.00 | 1.507 |
| 1:4:6 | 4 | 15.29 | 26.19 | 58.52 | 1.534 | | 50 | 2.00 | 26.00 | 72.00 | 1.534 |
| 1:5:6 | 5 | 14.35 | 30.72 | 54.93 | 1.547 | | 51 | 26.00 | 2.00 | 72.00 | 1.493 |
| 1:6:6 | 6 | 13.53 | 34.73 | 51.74 | (1) | | 52 | 27.18 | 2.00 | 70.82 | 1.496 |
| 1:8:6 | 7 | 12.12 | 41.51 | 46.37 | (1) | | 53 | 31.00 | 2.00 | 67.00 | 1.497 |
| 1:1:2 | 8 | 36.99 | 15.83 | 47.18 | 1.527 | | 54 | 28.46 | 15.00 | 56.54 | 1.515 |
| 1:2:2 | 9 | 31.94 | 27.34 | 40.72 | 1.554 | 2:2:9 | 55 | 23.27 | 9.96 | 66.77 | 1.500 |
| 1:2:3 | 10 | 26.53 | 22.71 | 50.76 | 1.531 | | 56 | 4.00 | 31.00 | 65.00 | 1.551 |
| 1:1:3(2) | 11 | 29.93 | 12.81 | 57.26 | 1.510 | | 57 | 31.68 | 16.00 | 52.32 | 1.517 |
| | 12 | 18.24 | 12.00 | 69.76 | 1.505 | | 58 | 40.12 | 5.00 | 54.88 | 1.508 |
| | 13 | 37.36 | 8.60 | 54.04 | 1.512 | | 59 | 32.00 | 6.00 | 62.00 | 1.503 |
| 2:1:8 | 14 | 26.57 | 5.68 | 67.75 | 1.501 | | 60 | 31.50 | 4.00 | 64.50 | 1.499 |
| 1:1:4 | 15 | 25.14 | 10.76 | 64.10 | 1.506 | | 61 | 27.50 | 8.50 | 64.00 | 1.500 |
| | 16 | 18.65 | 10.00 | 71.35 | 1.502 | | 62 | 25.00 | 9.50 | 65.50 | 1.501 |
| | 17 | 8.00 | 23.00 | 69.00 | 1.524 | | 63 | 24.48 | 7.50 | 68.02 | 1.497 |
| 2:2:5 | 18 | 33.09 | 14.16 | 52.75 | 1.517 | | 64 | 22.50 | 9.50 | 68.00 | 1.498 |
| | 19 | 7.00 | 18.00 | 75.00 | 1.512 | | 65 | 23.99 | 7.50 | 68.51 | 1.497 |
| | 20 | 13.00 | 10.00 | 77.00 | 1.495 | | 66 | 20.02 | 10.50 | 69.48 | 1.498 |
| 2:1:4 | 21 | 40.17 | 8.60 | 51.23 | 1.515 | | 67 | 19.50 | 6.00 | 74.50 | 1.493 |
| | 22 | 26.00 | 14.00 | 60.00 | 1.512 | | 68 | 17.00 | 6.50 | 76.50 | 1.490 |
| | 23 | 27.87 | 6.41 | 65.72 | 1.503 | | 69 | 22.91 | 7.50 | 69.59 | 1.497 |
| | 24 | 35.00 | 5.00 | 60.00 | 1.507 | 4:2:17 | 70 | 25.49 | 5.45 | 69.06 | 1.498 |
| 1:1:5(3) | 25 | 21.67 | 9.27 | 69.06 | 1.498 | 1:2:5 | 71 | 19.83 | 16.97 | 63.20 | 1.515 |
| 1:2:4 | 26 | 22.69 | 19.43 | 57.88 | 1.522 | 1:2:9 | 72 | 13.17 | 11.27 | 75.56 | 1.498 |
| | 27 | 10.00 | 10.00 | 80.00 | 1.494 | | 73 | 11.00 | 8.50 | 80.50 | 1.490 |
| | 28 | 7.00 | 15.00 | 78.00 | 1.502 | | 74 | 15.00 | 7.00 | 78.00 | 1.490 |
| | 29 | 11.00 | 13.00 | 76.00 | 1.503 | | 75 | 24.00 | 2.50 | 73.50 | 1.493 |
| | 30 | 19.00 | 4.00 | 77.00 | 1.490 | | 76 | 28.61 | 3.20 | 68.19 | 1.497 |
| | 31 | 41.76 | 2.86 | 55.38 | 1.510 | | 77 | 22.53 | 11.46 | 66.00 | 1.503 |
| | 32 | 34.00 | 3.00 | 63.00 | 1.506 | | 78 | 21.00 | 12.00 | 67.00 | 1.503 |
| | 33 | 29.49 | 9.61 | 60.90 | 1.509 | | 79 | 19.72 | 12.05 | 68.23 | 1.502 |
| | | | | | | | 80 | 5.50 | 12.50 | 82.00 | 1.496 |
| | 35 | 7.00 | 11.00 | 82.00 | 1.494 | | 81 | 9.00 | 8.50 | 82.50 | 1.488 |
| 1:2:8 | 36 | 14.38 | 12.30 | 73.32 | 1.504 | | 82 | 16.00 | 6.50 | 77.50 | 1.490 |
| | 37 | 16.00 | 8.00 | 76.00 | 1.493 | | 83 | 18.50 | 5.50 | 76.00 | 1.490 |
| | 38 | 11.00 | 5.00 | 84.00 | 1.483 | | 84 | 24.50 | 3.50 | 72.00 | 1.496 |
| | 39 | 7.00 | 9.00 | 84.00 | 1.487 | | 85-85a | 25.71 | 3.50 | 70.79 | 1.496 |
| | 40 | 4.00 | 17.00 | 79.00 | 1.505 | | 86 | 27.00 | 3.50 | 69.50 | 1.497 |
| | 41 | 15.00 | 5.00 | 80.00 | 1.495 | | 87 | 17.50 | 9.00 | 73.50 | 1.497 |
| | 42 | 22.00 | 4.00 | 74.00 | 1.495 | | 88 | 16.50 | 11.00 | 72.50 | 1.498 |
| | 43 | 21.00 | 8.00 | 71.00 | 1.497 | | 89 | 17.00 | 11.50 | 71.50 | 1.498 |
| | 44 | 24.00 | 5.00 | 71.00 | 1.497 | 1:3:10 | 90 | 11.55 | 14.83 | 73.62 | 1.503 |
| | 45 | 10.00 | 7.00 | 83.00 | 1.485 | | 91 | 37.78 | 5.64 | 56.78 | 1.508 |
| | 46 | 13.00 | 7.00 | 80.00 | 1.487 | | 92 | 34.14 | 8.97 | 56.89 | 1.508 |

TABLE 1 (*Continued*)

| Mol Ratio | Prep. | Per Cent $K_2O$ | Per Cent MgO | Per Cent $SiO_2$ | n of Glass | Mol Ratio | Prep. | Per Cent $K_2O$ | Per Cent MgO | Per Cent $SiO_2$ | n of Glass |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | 93 | 26.00 | 7.50 | 66.50 | 1.500 | | 114 | 30.00 | 2.00 | 68.00 | 1.497 |
| | 94 | 24.00 | 13.50 | 62.50 | 1.506 | | 115 | 30.00 | 4.00 | 66.00 | 1.499 |
| | 95 | 23.00 | 13.00 | 64.00 | 1.506 | 3:2:6 | 116 | 39.06 | 11.14 | 49.80 | 1.516 |
| | 96 | 19.84 | 13.31 | 66.85 | 1.505 | | 117 | 41.54 | 5.50 | 52.96 | 1.510 |
| | 97 | 20.45 | 11.00 | 68.55 | 1.500 | | 118 | 43.03 | 13.00 | 43.97 | 1.522 |
| 1:5:12 | 98-98a(4) | 9.27 | 19.83 | 70.90 | 1.517 | 2:1:3 | 119 | 46.08 | 9.86 | 44.06 | 1.522 |
| | 99 | 22.08 | 9.45 | 68.47 | 1.498 | | 120 | 45.80 | 25.00 | 29.20 | (1) |
| | 100 | 22.90 | 9.81 | 67.29 | 1.499 | 1:1:1 | 121-121a | 48.41 | 20.72 | 30.87 | 1.547(5) |
| | 101 | 23.73 | 10.16 | 66.11 | 1.500 | 2:1:2 | 122 | 54.01 | 11.56 | 34.43 | 1.527 |
| | 102 | 24.56 | 10.51 | 64.93 | 1.501 | | 123 | 59.23 | 3.00 | 37.77 | reacts |
| | 103 | 26.21 | 11.22 | 62.57 | 1.504 | | 124 | 37.80 | 14.00 | 48.20 | 1.519 |
| | 104 | 30.00 | 5.81 | 64.19 | 1.501 | | 125 | 41.10 | 6.50 | 52.40 | 1.512 |
| | 105 | 23.50 | 12.00 | 64.50 | 1.504 | | 126 | 36.39 | 11.63 | 51.98 | 1.514 |
| | 106 | 14.50 | 8.00 | 77.50 | 1.490 | | 127 | 35.00 | 14.00 | 51.00 | 1.517 |
| | 107 | 21.50 | 5.00 | 73.50 | 1.492 | | 128 | 46.78 | 13.12 | 40.10 | 1.525 |
| | 108 | 13.00 | 8.00 | 79.00 | 1.490 | | 129 | 60.46 | 1.00 | 38.54 | reacts |
| | 109 | 16.28 | 6.97 | 76.75 | 1.490 | | 130 | 52.00 | 2.00 | 46.00 | reacts |
| | 110 | 22.00 | 3.00 | 75.00 | 1.491 | | 131 | 44.81 | 4.00 | 51.19 | 1.515 |
| | 111 | 25.00 | 1.00 | 74.00 | 1.491 | | 132 | 40.00 | 20.00 | 40.00 | 1.531 |
| | 112 | 20.77 | 11.25 | 67.98 | 1.501 | | 133 | 44.07 | 16.95 | 38.98 | 1.528 |
| | 113 | 23.75 | 11.25 | 65.00 | 1.504 | | 134 | 11.50 | 16.00 | 72.50 | 1.509 |

(1) These batches would not melt completely within the limit of the furnaces (1600°).
(2) This batch has the composition of the compound $K_2O \cdot MgO \cdot 3SiO_2$.
(3) This batch has the composition of the compound $K_2O \cdot MgO \cdot 5SiO_2$.
(4) This batch has the composition of the compound $K_2O \cdot 5MgO \cdot 12SiO_2$.
(5) This batch has the composition of the compound $K_2O \cdot MgO \cdot SiO_2$.

As may be seen in table 1, a number of the compositions were made to have integral molecular ratios of the component oxides. This procedure helped considerably to locate the composition of the compounds during the early part of the work in that it eliminated many possible combinations from further consideration. Other compositions not having simple unit weight per cent ratios were made to fall on the various binary joins within the ternary system. Of these joins, those which illustrate partial or complete binary equilibrium at liquidus temperatures have been plotted in figure 6.

Whenever possible boundary-curve determinations were made (table 3), although the optical properties and crystallization habit of some of the phases precluded experimental determinations in certain cases.[23]

[23] For example, the boundary curve *A'B'* (fig. 5) could be determined only on batches lying in the $K_2O \cdot MgO \cdot 5SiO_2$ field as the tiny isotropic crystals of this phase in a glass of almost the same index of refraction were impossible to see if much of the finely divided, higher index, birefringent $K_2O \cdot MgO \cdot 3SiO_2$ was present.

TABLE 2

## DATA ON LIQUIDUS DETERMINATIONS

Abbreviations Used: L-large; M-moderate; S-small; VS-very small; R-rare; VR-very rare; VVR-exceedingly rare—right at the temperature of the phase change. These are rough visual estimates under the microscope, and are useful for comparison purposes only, as crystal habit and index of refraction may affect this estimate seriously.

| Preparation | *Above Liquidus Quenched sample all glass* Temp. °C | Time | *Below Liquidus Quenched sample contained crystals in glass* Temp. °C | Time | Amount of crystals |
|---|---|---|---|---|---|
| | Primary crystal phase—Cristobalite, $SiO_2$ | | | | |
| 40 | 1535 | 5 hrs. | 1530 | 4 hrs. | R |
| 50 | 1590 | 2 " | 1580 | 2 " | S |
| | Primary crystal phase—Tridymite, $SiO_2$ | | | | |
| 30 | 930 | 5 days | 925 | 3 days | R |
| 38 | 1325 | 48 hrs. | 1320 | 20 hrs. | S |
| 39 | 1485 | 5 " | 1480 | 19 " | VR |
| 41 | 1115 | 6 days | 1110 | 5 days | VR |
| 45 | 1320 | 20 hrs. | 1315 | 2 " | S |
| 46 | 1135 | 3 days | 1130 | 2 " | S |
| 73 | 1210 | 24 hrs. | 1205 | 24 hrs. | R |
| 74 | 985 | 5 days | 980 | 5 days | R |
| 81 | 1340 | 24 hrs. | 1335 | 54 hrs. | VR |
| 110 | 785 | 6 days | 780 | 3 days | VR(1) |
| 111 | 760 | 6 " | 755 | 2 " (2) | VR(1) |
| | Primary crystal phase—"Clinoenstatite," $MgO \cdot SiO_2$ (3) | | | | |
| 19 | 1480 | 2 hrs. | 1475 | 5 hrs. | R |
| 27 | 1310 | 6 " | 1305 | 4 days | R |
| 28 | 1465 | 5 " | 1460 | 6 hrs. | R |
| 29 | 1360 | 18 " | 1355 | 17 " | VR |
| 35 | 1420 | 6 " | 1415 | 17 " | S |
| 36 | 1265 | 4 days | 1260 | 4 days | VR |
| 72 | 1245 | 6 hrs. | 1240 | 22 hrs. | VR |
| 90 | 1380 | 23 " | 1375 | 19 " | S |
| | Primary crystal phase—Forsterite, $2MgO \cdot SiO_2$ | | | | |
| 2 | 1305 | 5 hrs. | 1300 | 5 hrs. | R |
| 3 | 1465(4) | 3 " | 1460 | 3 " | VR |
| 4 | 1545 | 1 " | 1540 | 1 " | R |
| 5 | 1600(4) | 1 " | 1590 | 1 " | S |
| 8 | 1215 | 3 " | 1210 | 24 " | R |
| 10 | 1480 | 3 " | 1475 | 2 " | S |
| 12 | 1130 | 24 " | 1125 | 4 days | R |
| 17 | 1495 | 6 " | 1490 | 6 hrs. | R |
| 22 | 1135 | 2 days | 1130 | 2 days | VVR |
| 26 | 1450 | 4 hrs. | 1445 | 6 hrs. | R |
| 49 | 1385 | 48 hrs. | 1380 | 20 " | R |
| 54 | 1170 | 6 " | 1165 | 15 " | S |
| 56 | 1535 | 5 " | 1530 | 4 " | S |

TABLE 2 (*Continued*)

| Preparation | *Above Liquidus Quenched sample all glass* Temp. °C | Time | *Below Liquidus Quenched sample contained crystals in glass* Temp. °C | Time | Amount of crystals |
|---|---|---|---|---|---|
| 57 | 1200 | 5½ hrs. | 1195 | 5 hrs. | R |
| 71 | 1355 | 3 days | 1350 | 14 " | R |
| 78 | 1065 | 2 " | 1060 | 5 days | VR |
| 79 | 1095 | 4 " | 1090 | 2 " | R |
| 94 | 1125 | 2 days | 1120 | 5 days | VR |
| 95 | 1110 | 2 " | 1105 | 4 " | VVR |
| 96 | 1190 | 21 hrs. | 1185 | 21 hrs. | R |
| (5)98 | 1470 | 6 " | 1465 | 6 " | R |
| (5)98a | 1465 | 2 " | 1460 | 10 " | S |
| (6)121a | 1540 | 1 " | 1530 | 1 " | R |
| 132 | 1410 | 1 " | 1400 | 1 " | R |
| 133 | 1365 | 1 " | 1355 | 1 " | S |
| 134 | 1395 | 14 " | 1390 | 10 " | R |
| | Primary crystal phase—$K_2O \cdot 5MgO \cdot 12SiO_2$ | | | | |
| 20 | 1175 | 1 day | 1170 | 5 days | S |
| 37 | 1020 | 4½ " | 1015 | 5 " | S |
| 47 | 1165 | 7 " | 1160 | 7 " | VR |
| 88 | 1135 | 4 " | 1130 | 2 " | S |
| 89 | 1140 | 4 " | 1135 | 4 " | VR |
| 106 | 1055 | 4 " | 1050 | 3 " | S |
| 108 | 1100 | 48 hrs. | 1095 | 12 hrs.(7) | R |
| | Primary crystal phase—$K_2O \cdot MgO \cdot 5SiO_2$ | | | | |
| 1 | 1060 | 7 days | 1055 | 4 days | S |
| 14 | 980 | 5 " | 975 | 4 " | S |
| 23 | 980 | 5 " | 975 | 4 " | S |
| 25 | 1090 | 11 hrs. | 1088 | 1 "(8) | 80% |
| 42 | 885 | 6 days | 880 | 3 " | S |
| 43 | 1080 | 2 " | 1075 | 2 " | S |
| 44 | 970 | 5 " | 965 | 3 " | S |
| 55 | 1080 | 2 " | 1075 | 3 " | R |
| 60 | 790 | 8 " | 785 | 6 " | R |
| 62 | 1055 | 3 " | 1050 | 3 " | S |
| 63 | 1055 | 3 " | 1050 | 3 " | S |
| 64 | 1085 | 2 " | 1084 | 2 " | R |
| 65 | 1060 | 3 " | 1055 | 3 " | S |
| 66 | 1070 | 4 " | 1065 | 7 " | S |
| 67 | 1010 | 4 " | 1005 | 4 " | S |
| 68 | 1005 | 5 " | 1000 | 2½ " | S |
| 69 | 1065 | 2 " | 1060 | 3 " | S |
| 70 | 985 | 5 " | 980 | 5 " | S |
| 75 | 765 | 7 " | 760 | 7 "(9) | VR |
| 76 | 835 | 6 " | 830 | 7 " | R |
| 77 | 1050 | 4 " | 1045 | 5 " | S |
| 82 | 995 | 6 " | 990 | 6 " | R |
| 83 | 975 | 5 " | 970 | 4 " | R |
| 84 | 860 | 5 " | 855 | 4 " | R |
| 85 | 865 | 4 " | 860 | 4 " | S |
| 85a | 865 | 4 " | 860 | 4 " | S |
| 86 | 860 | 5 " | 855 | 4 " | R |
| 87 | 1045 | 3 " | 1040 | 3 " | S |
| 93 | 1030 | 5 " | 1025 | 2 " | S |

TABLE 2 (*Continued*)

| Preparation | *Above Liquidus Quenched sample all glass* Temp. °C | Time | *Below Liquidus Quenched sample contained crystals in glass* Temp. °C | Time | Amount of crystals |
|---|---|---|---|---|---|
| 97 | 1065 | 6 days | 1060 | 5 days | S |
| 99 | 1084 | 2 " | 1082 | 4 " | S |
| 100 | 1080 | 2 " | 1075 | 5 " | S |
| 101 | 1070 | 2 " | 1065 | 2 " | VR |
| 102 | 1050 | 4 " | 1045 | 3 " | S |
| 105 | 1035 | 4 " | 1030 | 2 " | S |
| 107 | 955 | 2 " | 950 | 5 " | S |
| 109 | 1005 | 3 " | 1000 | 2 " | R |
| 112 | 1075 | 3 " | 1070 | 2 " | VR |
| 113 | 1045 | 2 " | 1040 | 4 " | S |
| 115 | 845 | 2 " | 840 | 4 " | S |
| | Primary crystal phase—$K_2O \cdot MgO \cdot 3SiO_2$ | | | | |
| 11 | 1135 | 2 days | 1133.5 | 2 days(10) | 80% |
| 13 | 1055 | 3 hrs. | 1050 | 20 hrs. | M |
| 15 | 1035 | 5 days | 1030 | 5 days | S |
| 18 | 1133.5 | 2 " | 1130 | 2 " | M |
| 24 | 885 | 2 " | 880 | 2 " | VR |
| 33 | 1095 | 2 " | 1090 | 20 hrs. | M |
| 59 | 935 | 17 hrs. | 930 | 5 days | S |
| 61 | 1000 | 2 days | 995 | 4 " | S |
| 91 | 965 | 5 " | 960 | 20 hrs. | R |
| 92 | 1080 | 3 " | 1078 | 2 days | M |
| 103 | 1080 | 3 " | 1075 | 3 " | R |
| 104 | 885 | 5 " | 880 | 3 " | S |
| | Primary crystal phase—$K_2O \cdot MgO \cdot SiO_2$, (?) | | | | |
| 21 | 1090 | 4 days | 1088 | 5 days | R |
| 116 | 1270 | 1 hr. | 1265 | 1 hr. | R |
| 118 | 1385 | 30 min. | 1380 | 15 min. | R |
| 119 | 1385 | 30 " | 1380 | 15 " | R |
| 122 | 1470 | 15 " | 1465 | 15 " | M |
| 123 | 1220 | 1 hr. | 1210 | 1 hr. | R |
| 124 | 1310 | 15 min. | 1305 | 15 min. | S |
| 125 | 985 | 1 hr. | 980 | 10 hrs. | R |
| 126 | 1140 | 1 day | 1135 | 1 day | S |
| 127 | 1210 | 1 hr. | 1200 | 1 hr. | R |
| 128 | 1450 | 15 min. | 1440 | 15 min. | S |
| 130 | 905 | 1 hr. | 900 | 1 hr. | VR |
| | Primary crystal phase—Periclase, MgO | | | | |
| 9 | 1600 | 1 hr. | 1595 | 1 hr. | R |
| | Primary crystal phase—$K_2O \cdot 4SiO_2$ | | | | |
| 51 | 740 | 12 days | 735 | 7 days | S |
| 52 | 739 | 9 " | 735 | 7 " | S |
| 75 | 725 | 2 " | 720 | 2 " | S(11) |
| 114 | 710 | 5 " | 705 | 5 " | M |

TABLE 2 (*Continued*)

| Preparation | *Above Liquidus Quenched sample all glass* Temp. °C | Time | *Below Liquidus Quenched sample contained crystals in glass* Temp. °C | Time | Amount of crystals |
|---|---|---|---|---|---|
| | | Primary crystal phase—$K_2O \cdot 2SiO_2$ | | | |
| 31 | 995 | 3 hrs. | 990 | 3 hrs. | S |
| 32 | 860 | 5 days | 855 | 4 days | R |
| 53 | 739 | 9 " | 735 | 7 " | R |
| 58 | 945 | 2½hrs. | 940 | 17 hrs. | S |
| 117 | 930 | 14½ " | 925 | 4 " | S |
| 131 | 920(4) | 1 hr. | 910 | 1 hr. | S |
| | | Primary crystal phase—$K_2O \cdot SiO_2$ | | | |
| 129 | 980 | 10 hrs. | 970 | 1 hr. | L |

(1) Metastable, only tridymite in the starting material.
(2) Held 4 days at 740° first.
(3) May include other modifications—see discussion in text.
(4) Quenched glass contained exceedingly rare crystals; right at the liquidus temperature.
(5) These preparations have the composition $K_2O \cdot 5MgO \cdot 12SiO_2$.
(6) This preparation was originally of the composition $K_2O \cdot MgO \cdot SiO_2$—see data on alkali losses.
(7) This result was duplicated in a run at 1090° for 4 days.
(8) This preparation has the composition $K_2O \cdot MgO \cdot 5SiO_2$.
(9) "Hydrothermally" crystallized material used. "Dry" crystallization yielded only $K_2O \cdot 4SiO_2$ crystals and hence a metastable liquidus determination.
(10) This preparation has the composition $K_2O \cdot MgO \cdot 3SiO_2$.
(11) Metastable; see footnote (9) above.

*Stability Fields for the Various Crystalline Phases of the Limiting Binary Systems.*—The fields of stability of the primary crystalline phases within the ternary system are shown in figures 3 and 5 and are labeled in figure 3.

*Cristobalite.*—The field of cristobalite (*IS'ANI*, fig. 5) extends from 1470° up to the melting point of cristobalite at 1713 ± 5° (Greig, 1927, p. 12). The crystals obtained at higher temperatures were usually rounded, though occasionally facetted masses showing very low birefringence and the characteristic complex twinning caused by the $\beta \rightarrow \alpha$ inversion were formed. The smaller crysals formed at lower temperatures appeared sensibly isotropic because of their size.

In that portion of the cristobalite field lying between *H'H* and the dashed curve in figure 5 two conjugate immiscible liquids are in equilibrium with cristobalite at appropriate temperatures between the temperature of *H'H* and that of the

TABLE 8

## DATA ON BOUNDARY CURVES

Abbreviations used:

| Phases— | | Amounts— | |
|---|---|---|---|
| Cris | Cristobalite, $SiO_2$ | L | large |
| Trid | Tridymite, $SiO_2$ | M | moderate |
| Clino | Clinoenstatite, $MgO \cdot SiO_2$, (1) | S | small |
| Forst | Forsterite, $2MgO \cdot SiO_2$ | VS | very small |
| Peric | Periclase, MgO | R | rare |
| 1:1:1 | $K_2O \cdot MgO \cdot SiO_2$ | VR | very rare |
| 1:1:3 | $K_2O \cdot MgO \cdot 3SiO_2$ | VVR | exceedingly rare, right at the temperature of the phase change |
| 1:1:5 | $K_2O \cdot MgO \cdot 5SiO_2$ | | |
| 1:5:12 | $K_2O \cdot 5MgO \cdot 12SiO_2$ | | |
| $KS_4$ | $K_2O \cdot 4SiO_2$ | | |
| $KS_2$ | $K_2O \cdot 2SiO_2$ | | |
| KS | $K_2O \cdot SiO_2$ | | |
| gl | glass | | |

| *Preparation* | *Temperature* | *Time* | *Phases present in quenched sample* (2) |
|---|---|---|---|
| | **Between Cristobalite and Clinoenstatite** | | |
| 40 | 1510 | 6 hrs. | M cris |
| | 1505 | 6 " | M cris and VR clino |
| 50 | 1535 | 3 " | M cris |
| | 1530 | 5 " | M cris and S clino |
| 80 | 1475 | 6 " | All gl |
| | 1470 | 6 " | S cris and R clino |
| | **Between Tridymite and Clinoenstatite** | | |
| 27 | 1240 | 4 days | L clino |
| | 1235 | 2 " | L clino and R trid |
| 35 | 1400 | 5 hrs. | M clino |
| | 1395 | 26 " | L clino and R cris (metastable) |
| 39 | 1380 | 20 " | L trid |
| | 1375 | 20 " | L trid and R clino |
| 73 | 1175 | 7 days | M trid |
| | 1170 | 7 " | M trid and VVR clino |
| 81 | 1275 | 3 " | M trid |
| | 1270 | 6 " | M trid and S clino |
| | **Between Tridymite and $K_2O \cdot 5MgO \cdot 12SiO_2$** | | |
| 45 | 1140 | 2 days | L trid |
| | 1135 | 3 " | L trid and S 1:5:12 |
| 46 | 1050 | 3 " | L trid |
| | 1045 | 4 " | L trid and VR 1:5:12 |
| 47 | 1135 | 3 " | L 1:5:12 |
| | 1130 | 2 " | L 1:5:12 and R trid |
| 106 | 975 | 4 " | L 1:5:12 |
| | 970 | 4 " | L 1:5:12 and R trid |
| 108 | 1075 | 3 " | L 1:5:12 |
| | 1070 | 2 " | L 1:5:12 and VR trid |
| | **Between Tridymite and $K_2O \cdot MgO \cdot 5SiO_2$** | | |
| 41 | 965 | 5 days | L trid |
| | 960 | 6 " | L trid and R 1:1:5 |
| 67 | 930 | 5 " | L 1:1:5 |
| | 925 | 3 " | L 1:1:5 and R trid |

TABLE 8 (*Continued*)

| *Preparation* | *Temperature* | *Time* | *Phases present in quenched sample* (2) |
|---|---|---|---|
| 68 | 980 | 5 days | L 1:1:5 |
| | 975 | 4 " | L 1:1:5 and VR trid |
| 74 | 980 | 5 " | R trid |
| | 975 | 5 " | M trid and M 1:1:5 |
| 82 | 990(3) | 6 " | R 1:1:5 |
| | 985(3) | 5 " | M 1:1:5 and M trid |
| 83 | 925 | 16 hrs. | L 1:1:5 |
| | 920 | 4 days | L 1:1:5 and S trid |
| | Between Tridymite (metastable) and $K_2O \cdot 4SiO_2$ | | |
| 111 | 750 | 4 days | R trid |
| | 745 | 4 " | R trid and R KS, |
| | Between Clinoenstatite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (Reaction curve) | | |
| 17 | 1175(4) | 7 days | L clino and VR 1:5:12 |
| | 1172(4) | 7 " | M clino and M 1:5:12 |
| 29 | 1170 | 7 " | L clino |
| | 1165 | 7 " | L clino and VR 1:5:12 |
| | 1160 | 7 " | L 1:5:12 |
| 36 | 1175 | 7 " | L clino |
| | 1170 | 7 " | R clino and L 1:5:12 |
| | 1165 | 7 " | L 1:5:12 |
| 49 | 1165 | 7 " | L clino |
| | 1160 | 7 " | L clino and M 1:5:12 |
| 72 | 1175(4) | 7 " | L clino |
| | 1172(4) | 7 " | R clino and L 1:5:12 |
| | 1170(4) | 7 " | L 1:5:12 |
| 98 | 1175(4) | 2 " | L clino |
| | 1170(4) | 3 " | L clino and VR 1:5:12 (Starting material "bombed" 1:5:12 crystals) |
| | Between Forsterite and Clinoenstatite (Reaction curve) | | |
| 17 | 1460 | 6 hrs. | L forst and VVR clino |
| | 1455 | 6 " | L forst and S clino |
| | 1395 | 26 " | L clino and R forst |
| | 1390 | 4 days | L clino |
| 48 | 1180 | 7 " | All glass |
| | 1175 | 7 " | S clino and R forst |
| | 1160 | 7 " | M clino and R forst |
| 49 | 1285 | 3 " | L forst |
| | 1280 | 3 " | L forst and L clino |
| | 1200 | 6 " | L clino and VR forst |
| | 1195 | 4 " | L clino |
| 56 | 1530 | 4 hrs. | S forst |
| | 1525 | 4 " | M forst and S clino |
| | 1485 | 5 " | VR forst and L clino |
| | 1480 | 4 " | L clino |
| 98 | 1455 | 6 " | S forst |
| | 1450 | 6 " | M forst and R clino |
| | 1400 | 24 " | L clino and VR forst |
| | 1395 | 12 " | L clino |

TABLE 3 (*Continued*)

| *Preparation* | *Temperature* | *Time* | *Phases present in quenched sample* (2) |
|---|---|---|---|
| 98a | 1445 | 7 hrs. | M forst |
| | 1440 | 19 " | M forst and M clino |
| | 1400 | 15 " | L clino and VVR forst |
| | 1390 | 10 " | L clino |
| 134 | 1390 | 10 " | R forst |
| | 1385 | 4 days | S clino |
| Between Forsterite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (Reaction curve) | | | |
| 2 | 1100 | 7 days | L forst |
| | 1095 | 7 " | L forst and R 1:5:12 |
| 12 | 1120 | 5 " | R forst |
| | 1115 | 5 " | VR forst and S 1:5:12 |
| | 1110 | 5 " | VR forst and M 1:5:12 |
| | 1105 | 4 " | M 1:5:12 |
| 49 | 1120 | 5 " | L 1:5:12 and S forst |
| | 1115 | 7 " | L 1:5:12 |
| 79 | 1070 | 7 " | M forst |
| | 1065 | 7 " | S forst and M 1:5:12 |
| | 1057 | 4 " | L 1:5:12 |
| Between Forsterite and $K_2O \cdot MgO \cdot 5SiO_2$ | | | |
| 77 | 1035 | 3 days | L 1:1:5 |
| | 1030 | 3 " | L 1:1:5 and M forst |
| 78 | 1055 | 4 " | R forst |
| | 1050 | 3 " | M forst and M 1:1:5 |
| 96 | 1055(5) | 4 " | M forst and L glass |
| | 1050(5) | 4 " | L forst, L 1:1:5, and no gl |
| 105 | 1030 | 2 " | S 1:1:5 |
| | 1025 | 2 " | L 1:1:5 and S forst |
| 112 | 1057(5) | 4 " | L 1:1:5 and L glass |
| | 1055(5) | 4 " | L 1:1:5, R forst, and L gl |
| | 1050(5) | 4 " | L 1:1:5, L forst, and VVR gl |
| Between Forsterite and $K_2O \cdot MgO \cdot 3SiO_2$ | | | |
| 10 | 1125 | 19 hrs. | L forst |
| | 1120 | 2 days | L forst and M 1:1:3 |
| 18 | 1115 | 7 " | L 1:1:3 |
| | 1110 | 5 " | L 1:1:3 and L forst |
| 22 | 1100 | 21 hrs. | M forst |
| | 1095 | 18 " | M forst and R 1:1:3 |
| 54 | 1132(6) | 2 days | L forst |
| | 1130(6) | 7 " | L forst and L 1:1:3 |
| 57 | 1125 | 19 hrs. | L forst |
| | 1120 | 2 days | L forst and M 1:1:3 |
| 94 | 1050 | 2 " | L forst |
| | 1045 | 3 " | L forst and S 1:1:3 |
| Between Forsterite and $K_2O \cdot MgO \cdot SiO_2$ (6a) | | | |
| 8 | 1110 | 4 days | L forst |
| | 1100 | 5 " | L forst and L 1:1:1 |
| 9 | 1260 | 7 " | L forst |
| | 1255 | 7 " | L forst and L 1:1:1 |
| Between Periclase and Forsterite (Reaction curve) | | | |
| 9 | 1525 | 2 hrs. | M peric and VR forst |
| | 1490 | 1 " | R peric and R forst |
| | 1480 | 3 " | M forst |

TABLE 8 (*Continued*)

| *Preparation* | *Temperature* | *Time* | *Phases present in quenched sample* (2) |
|---|---|---|---|
| | Between $K_2O$·MgO·$SiO_2$ and $K_2O$·$SiO_2$ (6a) | | |
| 122 | 920 | 1 hr. | L 1:1:1 |
| | 910 | 2 days | L 1:1:1 and R KS |
| 123 | 935 | 1 hr. | L 1:1:1 |
| | 925 | 4 hrs. | L 1:1:1 and S KS |
| | Between $K_2O$·MgO·$SiO_2$ and $K_2O$·$2SiO_2$ (6a) | | |
| 119 | 910(7) | 2 days | L 1:1:1 and L gl |
| | 905(7) | 3 " | L 1:1:1, S $KS_2$, and S gl |
| 125 | 910 | 2 " | L 1:1:1 |
| | 905 | 1 hr. | L 1:1:1 and L $KS_2$ |
| 130 | 730 | 1 " | L 1:1:1 |
| | 720 | 1 " | L 1:1:1 and S $KS_2$ |
| 131 | 910(7) | 1 " | S $KS_2$ |
| | 905(7) | 1 " | L $KS_2$ and R 1:1:1 |
| | Between $K_2O$·MgO·$SiO_2$ and $K_2O$·MgO·$3SiO_2$ (6a) | | |
| 116 | 1045 | 2 days | L 1:1:1 |
| | 1040 | 4 " | L 1:1:1: and L 1:1:3 |
| 118 | 995 | 6 " | L 1:1:1 |
| | 990 | 6 " | L 1:1:1 and M 1:1:3 |
| 124 | 1125 | 1 " | L 1:1:1 |
| | 1120 | 1 " | L 1:1:1 and R 1:1:3 |
| 127 | 1140 | 1 " | L 1:1:1 |
| | 1135 | 1 " | L 1:1:1 and L 1:1:3 |
| | Between $K_2O$·MgO·$3SiO_2$ and $K_2O$·$2SiO_2$ | | |
| 18 | 915 | 2 days | L 1:1:3 |
| | 910 | 42 hrs. | L 1:1:3 and S $KS_2$ |
| 24 | 875 | 3 days | M 1:1:3 |
| | 870 | 3 " | L 1:1:3 and R $KS_2$ |
| 31 | 920 | 24 hrs. | L $KS_2$ |
| | 915 | 20 " | L $KS_2$ and R 1:1:3 |
| 58 | 915 | 2 days | L $KS_2$ |
| | 910 | 42 hrs. | L $KS_2$ and R 1:1:3 |
| 59 | 820 | 7 days | L 1:1:3 |
| | 815 | 4 " | L 1:1:3 and R $KS_2$ |
| 91 | 935(8) | 17 hrs. | S 1:1:3 |
| | 931(8) | 17 " | L 1:1:3, L $KS_2$, and R gl |
| 92 | 935(8) | 17 " | L 1:1:3 and M gl |
| | 931(8) | 17 " | L 1:1:3, L $KS_2$, and R gl |
| | Between $K_2O$·MgO·$3SiO_2$ and $K_2O$·MgO·$5SiO_2$ | | |
| 55 | 1035(9) | 4 days | L 1:1:5 and L gl |
| | 1030(9) | 5 " | L 1:1:5, M 1:1:3, and R gl |
| 62 | 1030(9) | 3 " | L 1:1:5 |
| | 1025(9) | 3 " | L 1:1:5 and S 1:1:3 |
| 64 | 1025 | 3 " | L 1:1:5 and R gl |
| | 1020 | 10 " | L 1:1:5, S 1:1:3, and R gl |
| 93 | 860 | 5 " | L 1:1:5 |
| | 855 | 4 " | L 1:1:5 and R 1:1:3 |
| 100 | 1025 | 6 " | L 1:1:5 and S gl |
| | 1020 | 10 " | L 1:1:5, L 1:1:3, and R gl |
| 101 | 1030(9) | 5 " | L 1:1:5 and L gl |
| | 1025(9) | 6 " | L 1:1:5, S 1:1:3, and L gl |

TABLE 3 (*Continued*)

| *Preparation* | *Temperature* | *Time* | *Phases present in quenched sample* (2) |
|---|---|---|---|
| 102 | 1030(9) | 5 days | L 1:1:5 and L gl |
| | 1025(9) | 6 " | L 1:1:5, R 1:1:3, and L gl |
| 113 | 1025 | 2 " | S 1:1:5 |
| | 1020 | 10 " | L 1:1:5 and L 1:1:3 |
| | Between $K_2O \cdot MgO \cdot 5SiO_2$ and $K_2O \cdot 2SiO_2$ | | |
| 23 | 810 | 7 days | L 1:1:5 |
| | 805 | 9 " | L 1:1:5 and R $KS_2$ |
| 60 | 785 | 6 " | R 1:1:5 |
| | 780 | 3 " | S 1:1:5 and VR $KS_2$ |
| 115 | 745 | 2 " | S 1:1:5 |
| | 740 | 2 " | S 1:1:5 and R $KS_2$ |
| | Between $K_2O \cdot 2SiO_2$ and $K_2O \cdot 4SiO_2$ | | |
| 53 | 710 | 5 days | S $KS_2$ |
| | 705 | 5 " | S $KS_2$ and R $KS_4$ |
| 114 | 695 | 3 " | L $KS_4$ |
| | 690 | 5 " | L $KS_4$ and S $KS_2$ |
| | Between $K_2O \cdot MgO \cdot 5SiO_2$ and $K_2O \cdot 5MgO \cdot 12SiO_2$ | | |
| 12 | 1060 | 5 days | L 1:5:12 |
| | 1055 | 3 " | L 1:5:12 and S 1:1:5 |
| 16 | 1055 | 7 " | All glass |
| | 1050 | 7 " | S 1:1:5 and S 1:5:12 |
| 37 | 1000 | 2½ " | S 1:5:12 |
| | 995 | 4 " | S 1:5:12 and S 1:1:5 |
| 66 | 1065(10) | 7 " | L 1:1:5 |
| | 1060(10) | 5 " | L 1:1:5 and S 1:5:12 |
| 87 | 1040 | 3 " | S 1:1:5 |
| | 1035 | 5 " | M 1:1:5 and VR 1:5:12 |
| 88 | 1040 | 4 " | L 1:5:12 |
| | 1035 | 4 " | L 1:5:12 and VR 1:1:5 |
| 89 | 1050 | 3 " | L 1:5:12 |
| | 1045 | 3 " | L 1:5:12 and M 1:1:5 |
| 97 | 1060 | 3 " | L 1:1:5 |
| | 1058 | 3 " | L 1:1:5 and S 1:5:12 |

(1) May include other modifications—see discussion in text.
(2) Glass is present in all cases unless otherwise stated.
(3) These runs determine binary eutectic point Q.
(4) These runs determine binary reaction point T.
(5) These runs determine binary eutectic point Y.
(6) These runs determine binary eutectic point I'.
(6a) The isotropic crystals obtained in some of these runs may not be the compound $K_2O \cdot MgO \cdot SiO_2$, see footnote 49.
(7) These runs determine the minimum temperature of the binary eutectic point L'.
(8) These runs determine binary eutectic point E'.
(9) These runs determine binary eutectic point A'.
(10) These runs determine binary eutectic point V.

TABLE 4

## DATA ON TERNARY INVARIANT POINTS

(Abbreviations given at heads of tables 2 and 3. The compositions of the ternary points are given in table 5.)

| *Preparation* | *Temperature °C* | *Time* | *Phases present in quenched sample* (1) |
|---|---|---|---|
| **Reaction Point N—Cristobalite, Tridymite, Clinoenstatite, and liquid** | | | |
| 80 | 1475 | 6 hrs. | All glass |
| | 1470 | 6 " | S cris, R clino, and gl |
| **Reaction Point O—Tridymite, Clinoenstatite, $K_2O \cdot 5MgO \cdot 12SiO_2$, and liquid** | | | |
| 27 | 1170 | 7 days | L clino, S trid, and gl |
| | 1165 | 7 " | S clino, M trid, L 1:5:12, and gl |
| | 1160 | 7 " | VVR clino, M trid, L 1:5:12, and gl |
| 45 | 1140 | 2 " | L trid |
| | 1135 | 3 " | L trid and S 1:5:12 |
| 47 | 1165 | 7 " | All glass |
| | 1160 | 7 " | VR 1:5:12 |
| | 1135 | 3 " | L 1:5:12 |
| | 1130 | 2 " | M 1:5:12 and R trid |
| 73 | 1170 | 7 " | M trid, VVR clino, and gl |
| | 1165 | 7 " | M trid, M clino, R 1:5:12, and gl |
| | 1160 | 6 " | M trid, S 1:5:12, and gl |
| **Eutectic Point P—Tridymite, $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and liquid** | | | |
| 37 | 965 | 4 days | L 1:1:5, R 1:5:12, and M gl |
| | 960 | 6 " | L 1:1:5, R 1:5:12, (M trid?), and no gl |
| 74 | 975 | 5 " | M 1:1:5, M trid, and L gl |
| | 960 | 4 " | L 1:1:5, L trid, R 1:5:12, and S gl |
| 106 | 965 | 4 " | M 1:5:12, R trid, and L gl |
| | 960 | 4 " | M 1:5:12, M(?) trid, (L 1:1:5?), and S-R gl |
| **Eutectic Point R—Tridymite, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot 4SiO_2$, and liquid (metastable)** | | | |
| 75 | 765 | 7 days | All glass |
| | 760 | 7 " | VR 1:1:5 |
| | 725(2) | 2 " | All glass |
| | 720(2) | 2 " | S $K_2O \cdot 4SiO_2$ (metastable) |
| 111 | 720 | 5 " | L $KS_4$, L trid, and L glass |
| | 710 | 5 " | L KS, L trid, S(?) 1:1:5, and R gl |
| **Reaction Point U—Forsterite, Clinoenstatite, $K_2O \cdot 5MgO \cdot 12SiO_2$, and liquid** | | | |
| 48 | 1160 | 7 days | R forst, M clino, and glass |
| | 1155 | 7 " | S forst, S clino, S 1:5:12, and gl |
| | 1150 | 5 " | M 1:5:12 and glass |
| 49 | 1160 | 7 " | L clino, M 1:5:12, and gl |
| | 1155 | 7 " | L clino, VR forst, L 1:5:12, and gl |
| | 1150 | 7 " | R forst, L 1:5:12, and gl |
| 88 | 1135 | 4 " | All glass |
| | 1130 | 2 " | S 1:5:12 |
| 89 | 1140 | 4 " | All glass |
| | 1135 | 4 " | VR 1:5:12 |

TABLE 4 (*Continued*)

| *Preparation* | *Temperature °C* | *Time* | *Phases present in quenched sample* (1) |
|---|---|---|---|
| | Eutectic Point X—Forsterite, $K_2O \cdot 5MgO \cdot 12SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and liquid | | |
| 79 | 1040 | 4 days | L 1:5:12, S forst, L(?) 1:1:5, and L gl |
| | 1035 | 4 " | L 1:5:12, S forst, L(?) 1:1:5, and R gl |
| 97 | 1050 | 4 " | S 1:5:12, L 1:1:5, and S gl |
| | 1045 | 3 " | S 1:5:12, L 1:1:5, R(?) forst, and no gl |
| | Eutectic Point Z—Forsterite, $K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and liquid | | |
| 77 | 1015 | 3 days | L forst, L 1:1:5, and L gl |
| | 1010 | 2 " | L forst, L 1:1:5, L 1:1:3, and VR gl |
| 95 | 1015 | 3 " | L forst, and L gl |
| | 1010 | 3 " | L forst, L 1:1:3, L 1:1:5, and no gl |
| 105 | 1015 | 2 " | M forst, L 1:1:5, and L gl |
| | 1010 | 3 " | M forst, L 1:1:5, L 1:1:3, and R gl |
| 113 | 1015 | 10 " | S forst, L 1:1:5, L 1:1:3, and L gl |
| | 1010 | 3 " | S forst, L 1:1:5, L 1:1:3, and R gl |
| | Reaction Point B'—$K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot 2SiO_2$, and liquid | | |
| 59 | 810 | 7 days | L 1:1:3, S $KS_2$, and M gl |
| | 805 | 9 " | L 1:1:3, S $KS_2$, (M 1:1:5?), and S gl |
| | 800 | 8 " | L 1:1:3, S $KS_2$, (L 1:1:5?), and R gl |
| | 790 | 8 " | L 1:1:3, S $KS_2$, (L 1:1:5?), and no gl |
| 60 | 785 | 6 " | R 1:1:5 |
| | 780 | 3 " | S 1:1:5 and VR $KS_2$ |
| 93 | 815 | 4 " | L 1:1:5, R 1:1:3, and L gl |
| | 805 | 9 " | L 1:1:5, R 1:1:3, and R $KS_2$ |
| 104 | 885 | 5 " | All gl |
| | 880 | 3 " | S 1:1:3 in gl |
| | Eutectic Point C'—$K_2O \cdot MgO \cdot 5SiO_2$, $K_2O \cdot 4SiO_2$, $K_2O \cdot 2SiO_2$, and liquid | | |
| 53 | 710 | 5 days | S $KS_2$ |
| | 705 | 5 " | S $KS_2$ and R $KS_2$ |
| 76 | 835 | 6 " | All glass |
| | 830 | 7 " | R 1:1:5 in gl |
| 114 | 695 | 3 " | L $KS_2$ |
| | 690 | 5 " | L $KS_2$ and S $KS_2$ |
| 115 | 705 | 4 " | L $KS_2$ and R 1:1:5 |
| | 700 | 2 " | L $KS_2$, R $KS_2$, and R 1:1:5 |
| | Eutectic Point F'—$K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot MgO \cdot SiO_2$, $K_2O \cdot 2SiO_2$, and liquid (3) | | |
| 13 | 910 | 42 hrs. | L 1:1:3, S $KS_2$(?),1:1:1(?), and S gl |
| | 905 | 48 " | L 1:1:3, S $KS_2$(?), 1:1:1(?), and R gl |
| 31 | 910 | 48 " | S 1:1:3, L $KS_2$, and M gl |
| | 905 | 48 " | S 1:1:3, L $KS_2$, (S 1:1:1?), and no gl |
| 58 | 910 | 42 " | L $KS_2$, S 1:1:3, and S gl |
| | 905 | 48 " | L $KS_2$, M 1:1:3, (S 1:1:1?), and no gl |
| 116 | 910 | 2 days | L 1:1:1, L 1:1:3, and L gl |
| | 905 | 3 " | L 1:1:1, L 1:1:3, M $KS_2$, and M gl |
| | 900 | 12 hrs. | L 1:1:1, L 1:1:3, L $KS_2$, and R gl |
| 117 | 905 | 3 days | M $KS_2$, (1:1:1?), and M gl |
| | 900 | 16 hrs. | No glass |
| 124 | 905 | 3 days | L 1:1:1, L 1:1:3, and R gl |
| | 900 | 12 hrs. | L 1:1:1, L 1:1:3, R $KS_2$, and VR gl |

TABLE 4 (*Continued*)

| *Preparation* | *Temperature °C* | *Time* | *Phases present in quenched sample* (1) |
|---|---|---|---|
| 125 | 905 | 1 hr. | L 1:1:1, L $KS_2$, and L gl |
| | 900 | 1 " | L 1:1:1, L $KS_2$, (L 1:1:3?), and R gl |
| | Eutectic Point G'—$K_2O$·MgO·3$SiO_2$, $K_2O$·MgO·$SiO_2$, Forsterite, and liquid (3) | | |
| 8 | 1110 | 4 days | L forst and L gl |
| | 1100 | 5 " | L forst, L 1:1:1, and VR gl |
| 10 | 1110 | 5 " | L forst, L 1:1:3, and L gl |
| | 1105 | 2 " | L forst, L 1:1:3, (S 1:1:1?), and no gl |
| 18 | 1110 | 5 " | L forst, L 1:1:3, and S gl |
| | 1105 | 1 day | L forst, L 1:1:3, (S 1:1:1?), and R gl |
| | 1095 | 4 days | L forst, L 1:1:3, (S 1:1:1?), and no gl |
| 57 | 1110 | 2 " | L forst, L 1:1:3, and S-R gl |
| | 1105 | 2 " | L forst, L 1:1:3, (S 1:1:1?), and no gl |

(1) Most of these results were obtained by starting with the all-crystalline material. The intergrowths of very minute crystals with insufficiently distinctive optical properties prevented accurate determination of the presence of one of the three crystal phases at the ternary point in some cases. Reliance then had to be placed on sharp differences in the amounts of liquid (glass) formed in samples of the all-crystalline material held at various temperatures.

(2) Only $K_2O$·4$SiO_2$ crystals present in the glass at the start.

(3) The isotropic crystals obtained may not be the compound $K_2O$·MgO·$SiO_2$, see footnote 49.

TABLE 5

## SUMMARY OF INVARIANT POINTS

| Point (1) | | Equilibrium type | Crystal phases in equilibrium with liquid at point |
|---|---|---|---|
| W | UNARY | Melting | $K_2O \cdot MgO \cdot 5SiO_2$ |
| J′ | UNARY | " | $K_2O \cdot MgO \cdot 3SiO_2$ |
| O′ | UNARY | " | $K_2O \cdot MgO \cdot SiO_2$ (?) |
| Q | BINARY | Eutectic | Tridymite + $K_2O \cdot MgO \cdot 5SiO_2$ |
| T | BINARY | Reaction | Clinoenstatite + $K_2O \cdot 5MgO \cdot 12SiO_2$ |
| V | BINARY | Eutectic | $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 5MgO \cdot 12SiO_2$ |
| Y | BINARY | " | $K_2O \cdot MgO \cdot 5SiO_2$ + Forsterite |
| A′ | BINARY | " | $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot MgO \cdot 3SiO_2$ |
| D′ | BINARY | " | $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 4SiO_2$ |
| E′ | BINARY | " | $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot 2SiO_2$ |
| I′ | BINARY | " | $K_2O \cdot MgO \cdot 3SiO_2$ + Forsterite |
| L′ | BINARY | " | $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$ |
| N′ | BINARY | " | $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot SiO_2$ |
| P′ | BINARY | ? | $K_2O \cdot MgO \cdot SiO_2$ (?) + Periclase |
| G″ | BINARY | Eutectic? | $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot MgO \cdot 3SiO_2$ |
| N | TERNARY | Inversion | Clinoenstatite + Cristobalite + Tridymite |
| O | TERNARY | Reaction | Clinoenstatite + Tridymite + $K_2O \cdot 5MgO \cdot 12SiO_2$ |
| P | TERNARY | Eutectic | Tridymite + $K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ |
| R | TERNARY | " (3) | Tridymite + $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 4SiO_2$ |
| U | TERNARY | Reaction | Forsterite + Clinoenstatite + $K_2O \cdot 5MgO \cdot 12SiO_2$ |
| X | TERNARY | Eutectic | Forsterite + $K_2O \cdot 5MgO \cdot 12SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ |
| Z | TERNARY | " | Forsterite + $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ |
| B′ | TERNARY | Reaction | $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 2SiO_2$ |
| C′ | TERNARY | Eutectic | $K_2O \cdot MgO \cdot 5SiO_2$ + $K_2O \cdot 2SiO_2$ + $K_2O \cdot 4SiO_2$ |
| F′ | TERNARY | " | $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$ |
| G′ | TERNARY | " | $K_2O \cdot MgO \cdot 3SiO_2$ + $K_2O \cdot MgO \cdot SiO_2$ (?) + Forsterite |
| K′ | TERNARY | Reaction | $K_2O \cdot MgO \cdot SiO_2$ (?) + Forsterite + Periclase |
| M′ | TERNARY | Eutectic | $K_2O \cdot MgO \cdot SiO_2$ (?) + $K_2O \cdot 2SiO_2$ + $K_2O \cdot SiO_2$ |

(1) See figure 5.

(2) The compositions of the invariant points were obtained mainly by extension of the established boundary curves to intersection. The compositions are in weight per cent, as are the approximate limits. In those cases where one component is present in considerably smaller quantities than the others, the limit of error is probably less than the figure given for that component.

(3) Metastable.

TABLE 5 (*Continued*)

SUMMARY OF INVARIANT POINTS

| Point (1) | Composition (2) | | | | Temperature °C |
|---|---|---|---|---|---|
| | $K_2O$ per cent | MgO per cent | $SiO_2$ per cent | Approx. limits ± per cent | |
| W | 21.66 | 9.27 | 69.06 | — | 1089 ± 1 |
| J′ | 29.93 | 12.81 | 57.25 | — | 1134 ± 1 |
| O′ | 48.41 | 20.72 | 30.87 | — | (1650 ±) |
| Q | 15.5 | 6.7 | 77.8 | 0.3 | 987 ± 5 |
| T | 13.5 | 10.5 | 76.0 | 0.3 | 1174 ± 2 |
| V | 20.0 | 10.7 | 69.3 | 0.2 | 1063 ± 3 |
| Y | 20.5 | 11.8 | 67.7 | 0.2 | 1053 ± 2 |
| A′ | 24.8 | 10.7 | 64.5 | 0.2 | 1030 ± 5 |
| D′ | 26.5 | 2.4 | 71.1 | 0.3 | 730 ± 5 |
| E′ | 38.3 | 5.2 | 56.5 | 0.5 | 933 ± 5 |
| I′ | 29.5 | 13.5 | 57.0 | 0.2 | 1131 ± 1 |
| L′ | 44.8 | 4.2 | 51.0 | 1.0 | 910 ± ? |
| N′ | 60.1 | 1.7 | 38.2 | 0.5 | 950 ± ? |
| P′ | — | — | — | — | >1650 ± ? |
| G″ | 33.0 | 14.0 | 53.0 | 1.0 | 1110 ± 20? |
| N | 5.7 | 12.3 | 82.0 | 0.5 | 1470 ± ? |
| O | 11.6 | 8.8 | 79.6 | 0.3 | 1165 ± 2 |
| P | 15.1 | 7.2 | 77.7 | 0.3 | 963 ± 3 |
| R | 24.5 | 2.0 | 73.5 | 0.3 | 715 ± 10 |
| U | 16.4 | 11.5 | 72.1 | 0.3 | 1155 ± 2 |
| X | 20.2 | 11.8 | 68.0 | 0.2 | 1042 ± 7 |
| Z | 23.9 | 12.0 | 64.1 | 0.2 | 1013 ± 3 |
| B′ | 31.6 | 4.8 | 63.6 | 0.5 | 795 ± 15 |
| C′ | 30.0 | 2.5 | 67.5 | 0.3 | 685 ± 20 |
| F′ | 40.5 | 6.0 | 53.5 | 0.5 | 905 ± 5 |
| G′ | 33.0 | 15.0 | 52.0 | 1.0 | 1105 ± 10 |
| K′ | 36.0 | 22.0 | 42.0 | 4.0 | 1350 ± 50 |
| M′ | 54.2 | 0.5 | 45.3 | 1.0 | 720 ± ? |

minimum temperature on the dashed curve. No data are available on the extent of this two-liquid field into the ternary system from the MgO-$SiO_2$ side other than that by interpolation of isotherms from points on the sidelines and compositions 39, 40, 50, and 80. To these must be added Greig's point at 4.4 per cent $K_2O$, 10.6 per cent MgO, and 85.0 per cent $SiO_2$[24] which had a cristobalite liquidus at 1541 ± 9°,

[24] All per cent figures refer to weight per cent.

and melted to one liquid (Greig, 1927, p. 40). The above data make any extension of the two-liquid field beyond 2 per cent $K_2O$ improbable, and the agreement of the isotherms drawn from the above with the data on the system $Na_2O$-MgO-$SiO_2$ (Greig, 1927, p. 35) is sufficiently good to warrant the assumption that the field of two liquids extends about the same amount or even less into the $K_2O$ system (*i.e.*, to about 1.5 per cent $K_2O$ or less). This is to be expected in view of the weakly polarizing nature of the $K^+$ ion which aids the formation of oxygen bridges and hence tends to eliminate liquid immiscibility (Barth and Rosenqvist, 1949).

*Tridymite.*—The field of tridymite extends from 1470° down to the eutectic point *R* (*NABRQPON*, fig. 5) at 715 ± 10°. Thus it extends metastably over an area where quartz should be the stable form. Since $K_2O$ and MgO are not known to enter the quartz lattice, but may well be present in appreciable quantities in the tridymite lattice (Lukesh, 1942, found approximately 21 per cent CaO, $Na_2O$, and $Al_2O_3$ in tridymite from Plumas Co., this tridymite having the empirical formula $NaCaAl_3Si_{15}O_{36}$), the inversion, under equilibrium conditions, should be lowered an appreciable amount below 867° wherever it can occur in the ternary system. No quartz formed in any of the mixtures, although a number were crystallized at temperatures below the 867° (Kracek, 1939) inversion of tridymite to quartz, and two had their metastable tridymite liquidus considerably below 867° (110 and 111). Presumably these would have a higher temperature stable quartz liquidus if held for a longer period, but as these glasses are exceedingly viscous they might require excessive time.[25]

The difference between the metastable tridymite and the higher temperature stable quartz liquidus is unknown in this system, but its magnitude may be judged from several experimental determinations of it in binary systems. In the system $K_2O$-$SiO_2$ the metastable tridymite-$K_2O \cdot 4SiO_2$ eutectic is only 2° lower than the stable quartz-$K_2O \cdot 4SiO_2$ eutectic (Kracek, Bowen, and Morey, 1937), and in the system $Na_2O$-$SiO_2$ the metastable eutectic of $Na_2O \cdot 2SiO_2$ with tridymite is 11° below the stable eutectic with quartz (Kracek, 1930b). These small differences in the eutectic temperature may be

[25] Three-month crystallization of 110 at temperatures of 800° and 720° failed to yield quartz crystals.

misleading, however, as the difference between the stable liquidus temperature of quartz and the metastable one of tridymite for a given composition is much greater because of the steep slope of the silica liquidus and lateral shift in the eutectic point. When the data for these two systems are plotted on an enlarged scale, the metastable tridymite liquidus is found to be lower than that of stable quartz by amounts varying from 0° (at the 870° inversion point) to as much as 50° for compositions at the metastable eutectic.

The tridymite crystals formed were exceedingly thin hexagonal flakes; the size and speed of crystallization varied with the temperature of formation.

*Clinoenstatite.*—The field of the pyroxene clinoenstatite (*INOTUJI*, fig. 5) is unusual in the degree to which it encroaches upon the area where silica might be expected. A composition to the right of *N* (fig. 5) can have over 82.5 per cent $SiO_2$ and only 10 per cent MgO in it and still form the pyroxene clinoenstatite (composition 59.9 per cent $SiO_2$ and 40.1 per cent MgO) as the primary phase. Three of the other alkali-alkaline earth-silica systems, $Na_2O$-CaO-$SiO_2$ (Morey and Bowen, 1925), $K_2O$-CaO-$SiO_2$ (Morey, Kracek, and Bowen, 1930), and $Na_2O$-MgO-$SiO_2$ (Botvinkin and Popova, 1937; Manuilova, 1937), are similar, but the most siliceous liquid from which the pyroxenoid pseudowollastonite (CaO·$SiO_2$) can form as the the primary phase is only 75 per cent $SiO_2$ in the first and 76 per cent in the second; the pyroxene clinoenstatite separates out from certain compositions with as much as 77 per cent $SiO_2$ in the third of these systems. Other ternary systems of silica with $K_2O$ and $Na_2O$ (Kracek, 1932), with diopside and leucite (Schairer and Bowen, 1938), with anorthite and leucite (Schairer and Bowen, 1947b), and with forsterite and leucite (Schairer, 1948) show similar tendencies but to a lesser degree.

The field of clinoenstatite is rather narrow, as may be seen from figure 5 and the following example: a mixture of the composition 68 per cent $SiO_2$, 32 per cent MgO (on the MgO-$SiO_2$ binary) has a cristobalite liquidus at 1660° (Greig, 1927, p. 17). The addition of 1 per cent $K_2O$ to this composition will cause it to form clinoenstatite as the primary phase, with a liquidus of 1540°, and the addition of 2.7 per cent more $K_2O$ (3.7 per cent total) will cause it to form forsterite as

the primary phase, with a liquidus of 1533°. Compositions near to the clinoenstatite-silica eutectic on the $MgO$-$SiO_2$ binary (at 65 per cent $SiO_2$, 35 per cent MgO) need the addition of only about 2 per cent $K_2O$ to change them from a cristobalite to a forsterite liquidus.

The strong curvature of the clinoenstatite-tridymite boundary curve (fig. 5) results in a rapid change in the bulk composition of the crystals forming at any given $-\Delta T$ along this boundary curve, *e.g.*, from 87 per cent clinoenstatite, 13 per cent tridymite at point *N* to 13 per cent clinoenstatite, 87 per cent tridymite just above point *O*, as shown by the intersection of the tangent to the boundary curve with *KS'*.

The crystal habit of the clinoenstatite varied widely. In the high-temperature compositions (>1300° ±) the crystals were short, stubby prisms (almost equant) with the forms (100), (010), (110), and (111), an extinction angle ($Z \wedge c$) of 22°, the characteristic multiple twinning on (100) (Allen, Wright, and Clement, 1906), and pronounced rough cracks parallel to (001) (Bowen and Andersen, 1914). At lower temperatures (875-1300 ±) those compositions which lie in the "Clinoenstatite" field of figure 3 crystallized to extremely thin needles elongated parallel to the slow vibration direction (+ elongation) with parallel extinction, and with multiple twinning absent throughout.[26] In a number of preparations these acicular crystals were formed metastably in the first few minutes at the start of crystallization, only to disappear after a few weeks in the furnace.

It might appear that this system would offer good possibilities of clarifying the confusion that exists concerning the various forms of the compound $MgO \cdot SiO_2$, but up to the present it has not done so. The monoclinic form clinoenstatite has been obtained from melts with various fluxes in good crystals suitable for goniometry (Allen, Wright and Clement, 1906). Good crystals of the orthorhombic form enstatite have not been obtained in the laboratory.[27] Grigor'ev (1935) found

[26] In the system $MgO$-$Al_2O_3$-$SiO_2$ the clinoenstatite crystals formed were "seldom twinned" although 1345° was the lowest liquidus temperature involved. See Rankin and Merwin, 1918, footnote 2, p. 302.

[27] The second orthorhombic form of $MgO \cdot SiO_2$ obtained by Allen *et al.*, p. 400 and 433, similar to Kupfferite, was later shown to be a submicroscopic intergrowth of forsterite crystals and a siliceous glass, the mass having the composition $MgO \cdot SiO_2$ and the optical properties of a homogeneous substance. See Bowen and Posnjak, 1931.

that the addition of $CaF_2$ was necessary to cause enstatite to form on cooling a mixture of the composition $3MgO \cdot CaO \cdot 3SiO_2$. Bowen and Schairer (1935) caused new crystals of orthorhombic $(Mg, Fe)O \cdot SiO_2$ to form by the recrystallization of natural bronzites, but only with the aid of a small amount of NaF. Thilo (1937) converted "metatalc" (from the thermal decomposition of talc) to enstatite at 790° by the addition of LiF. The only syntheses of enstatite not involving the use of a flux seem to be formation both from a glass of the composition $MgO \cdot SiO_2$ at 1000-1100° (Allen, Wright, and Clement, 1906, p. 400) and from thermal decomposition of natural anthophyllite and talc (Thilo and Rogge, 1939; Rigterink, 1947). The former "enstatite" occurred as acicular crystals in the glass and had definitely parallel extinction in all orientations,[28] this being the only criterion then available to identify it as enstatite. Some of the preparations in the present study formed similar length-slow (*i.e.*, with *Z* vibration direction parallel to the long axis) acicular crystals with definitely parallel extinction, but as the temperatures were considerably above the 1140° inversion, these crystals cannot be enstatite. In those cases where thicker crystals grew (mostly above 1300°) they usually were of inclined extinction and hence presumably clinoenstatite. Bowen and Schairer (1935) give some evidence for an enantiotropic relation between enstatite and clinoenstatite with an inversion at about 1140°, enstatite being the stable form at <1140°. The reaction rate at temperatures near the inversion temperature is small. Four hours at 1150° were required to effect even a partial transformation. This inversion temperature is for the pure compound; the possibility is not excluded that small amounts of $K_2O$ may enter the pyroxene lattice in the present system and affect the inversion temperature slightly.

Enstatite would not be expected to appear at the liquidus surface in the present system on the basis of this inversion to clinoenstatite, as all liquids from which $MgO \cdot SiO_2$ can crystallize complete their crystallization above that temperature (*i.e.*, at *O*, 1165 ± 2°, or at *U*, 1155 ± 2°, see fig. 5). Under equilibrium conditions this inversion should take place in the solid state when these compositions are held at temperatures

[28] Allen *et al.* (1906), have shown that this precaution is necessary due to the occasional tabular habit of clinoenstatite crystals parallel to (100) yielding parallel extinction.

below 1140°, but no unequivocal evidence was found here to prove it, probably due to the slow rate.

Above 1400° there seems to be little doubt that clinoenstatite is the only stable phase, and all other forms, regardless of their source, invert to it, the differences being due to different starting materials, the rate factor (Allen, Wright, and Clement, 1906, above 1300°; Haraldsen, 1930, above 1400°?; Ewell, Bunting, and Geller, 1935, between 1200° and 1300°; Büssem and Schusterius, 1938, above 1400°; Thilo, 1939, above 1270°; Thilo and Rogge, 1939, above 1270°; and Eitel, 1943, above 1200°), and impurities (Rigterink, 1947; Haraldsen, 1930, reported rather large amounts of impurities in the $SiO_2$ and MgO used). Below these temperatures there appear to be forms of $MgO \cdot SiO_2$ other than enstatite and clinoenstatite. Haraldsen (1930) found, on the basis of X-ray data, that by heating talc a new form of $MgO \cdot SiO_2$ developed. Ewell, Bunting, and Geller (1935) did not duplicate the results of Haraldsen, but Thilo (1939) and Büssem and Schusterius (1938) did verify them, and in later work (1939) on anthophyllite and talc Thilo and Rogge discovered two other new forms, "$M_1$" and "$M_2$," in addition to the form found by Haraldsen.[29] There seems to be little doubt that at least some of these forms are metastable. Mesoenstatite is not stable at room temperatures, as Büssem *et al.* (1939) and later workers (Thurnauer and Rodriguez, 1942) found that grinding to prepare samples for X-ray work will cause mesoenstatite (protoenstatite) to invert to clinoenstatite unless 25 to 50 per cent of glass is present to stabilize it. Clark (1946) reports that mesoenstatite inverts spontaneously within two months at room temperature to form clinoenstatite with a volume change sufficient to crumble a fired briquette. Büssem and Schusterius (1938) found that various fluxes, such as $H_2O$, $Li_2O$, $CaF_2$, $H_3BO_3$, and borax, aided the change to clinoenstatite, and the inversion seems to be irreversible (Eitel, 1943).

In the present investigation a number of the samples which showed parallel extinction needles were X-rayed by the powder technique, but because of the distance between the composition points of the mixtures and that of $MgO \cdot SiO_2$ the necessarily small percentage of crystals present in the glass in each case

[29] The original form found by Haraldsen and the "metatalc" of Thilo appear to be identical with the "protoenstatite" of Büssem and of Eitel, and the "mesoenstatite" of Thilo and Rogge, and of later workers.

yielded rather poor patterns, and unfortunately the patterns of all forms of $MgO \cdot SiO_2$—clinoenstatite, enstatite, mesoenstatite, $M_1$, and $M_2$—are rather similar in some respects. However, several of the patterns obtained were very much more like that given by Clark for mesoenstatite than those for clinoenstatite or enstatite. A more thorough check on the optical properties of the $MgO \cdot SiO_2$ crystals obtained in the various preparations and more detailed X-ray work are planned. Recently, while the present paper was in press, W. R. Foster presented a paper on X-ray and thermal data at the meeting of the Geological Society of America in Washington, D. C., November 1950, indicating that protoenstatite (mesoenstatite) is the stable form at moderate and high temperatures but that it inverts during the cooling cycle to clinoenstatite in a manner similar to the inversion of high to low cristobalite.

*Forsterite.*—The field of forsterite covers a large part of the diagram (*LJUYI'G'K'ML*, fig. 5). Its extension toward the $SiO_2$ apex (up to 72.7 per cent $SiO_2$ near *U*, fig. 5) is similar to that of clinoenstatite but not as pronounced. The isotherms on the forsterite field above 1600° are only approximations up to the melting point of forsterite at 1890° ± 20° (Bowen and Andersen, 1914), as excessive volatilization of the platinum winding at higher temperatures makes 1600° the useful working limit of the furnaces.

The crystals of forsterite formed at high temperatures were nearly equant, sharp prisms, usually showing the forms (100), (010), (101), (021), (001), and (111). At lower temperatures (near the line *UZI'G'*, fig. 5) the forsterite crystals are usually very thin plates, blades, or needles, with the *Z* vibration direction parallel to the elongation (length-slow, or + elongation). Although many of these plates and blades were elongated to five times their width, the direction of elongation was frequently not parallel to any one of the crystallographic axes, resulting in inclined extinction of as much as 40°. Although these crystals were very thin, the elongation appeared to be due to excessive development of diagonally opposite faces of (011) or (101).

*Periclase.*—Only one composition was situated on the periclase liquidus surface (9), although indirect evidence from 120 and 121 is concordant with the data from it. Both of these

latter compositions yielded tiny sharp octahedra of periclase, an unusual habit for this mineral since it normally crystallizes from melts as completely rounded grains.[30] X-ray examination of this material verified the petrographic examination. In certain mixtures in this system periclase will form as the primary phase with as much as 45 to 46 per cent $SiO_2$ present. Presumably there is a smooth rise in the liquidus surface of periclase up to its melting point at 2800° (Kanolt, 1913; Ruff, 1913, melting point >2500°).

*Potassium Silicates.*—The fields of the potassium silicates $K_2O{\cdot}4SiO_2$, $K_2O{\cdot}2SiO_2$, and $K_2O{\cdot}SiO_2$ are small, extending out into the ternary system to only 2½, 6, and 2 per cent MgO respectively, because of the low melting points of these three silicates and the formation of three ternary compounds with a 1:1 ratio of $K_2O$:MgO. Compositions having $K_2O{\cdot}4SiO_2$ as the primary phase (area *CBRD'C'DC*, fig. 5) were very reluctant to crystallize, although they eventually formed thin blades and needles of $K_2O{\cdot}4SiO_2$ characterized by their low indices and low birefringence. Compositions having a $K_2O{\cdot}2SiO_2$ liquidus (area *EDC'B'F'M'FE*, fig. 5) crystallized readily (in a few hours or days) to yield booklets of plates, occasionally of parallelogram outline with the optic plane in the plane of the tablet and the Z vibration direction bisecting the acute angle. Similar crystals have been described by Niggli (1913) and by Morey (1914). The $K_2O{\cdot}SiO_2$ field is very narrow and only one composition was made in it. As no composition was made with a $K_2O$:$SiO_2$ ratio >1, nothing can be said about the appearance of the orthosilicate $2K_2O{\cdot}SiO_2$ in the system (Kröger and Fingas, 1933).

*Stability Fields of the Ternary Compounds.*

*$K_2O{\cdot}MgO{\cdot}SiO_2$ (?).*

The field of this compound occupies a rather large area in the lower portion of the diagram (*P'K'G'G''F'L'M'N'*,

[30] This rounded growth of crystals seems to be most frequently found in very slightly undercooled melts; perhaps the slight oscillation in temperature due to the normal regulator action is sufficient to result in repeated minor solution and redeposition, with very slight undercooling. The preparations yielding the euhedral crystals of periclase were heated in a gas-fired furnace, not controlled by a regulator. For a discussion of this rounded growth of crystals see Naken (1915, 1917) and Tammann (1925). Sharp octahedra of MgO have been obtained from melts containing no silica (Rankin and Merwin, 1916).

fig. 5). It occurs usually as colorless transparent rounded grains, isotropic, with n = approximately 1.54, and a strong, distinctive X-ray powder pattern. Many of these grains possessed a small gas-filled cavity at the center, and occasionally sharp octahedra or skeletal growths consisting of three thin, mutually perpendicular dendrites were formed. There were some discrepancies in the measurement of the index of refraction from sample to sample; these may be due mainly to reaction of these high alkali materials with the index liquid, or they may be connected with the observed variation in the unit cell dimensions (see under X-ray Data). Another possibility is that some of these crystals were the compound $K_2O \cdot MgO \cdot 2SiO_2$ (see footnote 49).

The evidence is in favor of the composition of most of these isotropic crystals being $K_2O \cdot MgO \cdot SiO_2$, but is not adequate to state so definitely because of the high melting temperatures and the high alkali losses in this area of the diagram. When a mixture of the composition $K_2O \cdot MgO \cdot SiO_2$ was made up and held at 1620° for 30 minutes,[31] the batch was found to consist of a mass of round, clear, isotropic crystals with a small amount of interstitial glass and undissolved MgO. Remelting at 1650° for 10 minutes resulted in fusion and on cooling a dendritic mass of the same isotropic crystals with more glass was found. MgO was present also but had recrystallized to the sharp octahedra mentioned under "Periclase." Further fusion of a small sample of this batch for 5 seconds in an oxy-gas flame resulted in visible alkali fumes and the appearance of an appreciable quantity of forsterite crystals in the melt, along with the MgO and isotropic crystals. This behavior is caused by the loss of alkali changing the composition of the batch. In one case one 15 minute fusion in air at 1600° resulted in a drop of the $K_2O$ content from the weighed 48.4 per cent down to 28.1 per cent (determined by weight loss). Other attempts to synthesize this compound gave similar results. Batch 120, calculated to give approximately 95 per cent $K_2O \cdot MgO \cdot SiO_2$, 5 per cent MgO, showed the same behavior, but the amount of periclase in the fused material was definitely greater than in 121.

The above data indicate $K_2O \cdot MgO \cdot SiO_2$ to be the probable

[31] Using a gas-fired furnace and a Leeds and Northrup disappearing filament-type optical pyrometer.

composition of the compound and 1650° its approximate melting point, although the possibility of incongruent melting to MgO and liquid is not excluded. More accurate work will presumably require the control of the rather high alkali vapor pressures. Several other batches of integral molecular composition in the general area (with the ratios 2:1:2, 2:1:3, 2:1:4, 1:1:2, and 3:2:6 potash to magnesia to silica) were made up but cannot be the isotropic compound since they gave much lower liquidus determinations with the isotropic crystals as the primary phase, wide melting ranges, and definitely heterogeneous crystalline products. One of these ratios (2:1:3) occurs as an isometric compound in the systems $K_2O$-CaO-$SiO_2$ (Morey, Kracek, and Bowen, 1930), $Na_2O$-CaO-$SiO_2$ (Morey and Bowen, 1925), and possibly $K_2O$-ZnO-$SiO_2$ (Ingerson, Morey, and Tuttle, 1948), but the data on a batch of that composition (119) and neighboring points would seem to preclude both the possibility that that is the composition of the isotropic crystals in the present system and the possibility that such a compound occurs above the solidus in this system.

Apparently the counterpart of $K_2O \cdot MgO \cdot SiO_2$ does occur in the potash-zinc oxide-silica system in which an isotropic compound tentatively identfied as $K_2O \cdot ZnO \cdot SiO_2$ was found (Ingerson, Morey, and Tuttle, 1948, p. 33). The similarity of ionic size of $Zn^{++}$ and $Mg^{++}$ (0.83 and 0.78 Å) should result in similar structures for these two compounds. The substitution of the larger $Ca^{++}$ ion (1.06 Å) for $Mg^{++}$ cannot be made without changing the lattice, however, as the compound $K_2O \cdot CaO \cdot SiO_2$ is hexagonal (Morey, Kracek, and Bowen, 1930), and the substitution of the still larger $Pb^{++}$ ion (1.32 Å) apparently cannot be made at all (Geller and Bunting, 1936; McMurdie, 1941). The smaller sodium ion (0.98 Å) can presumably replace the larger potassium (1.33 Å), as the compound $Na_2O \cdot MgO \cdot SiO_2$ is isometric also (Botvinkin and Popova, 1937; Manuilova, 1937) and the substitution of $2Al^{+++}$ for $Mg^{++}$ and $Si^{++++}$ results in the compound $K_2O \cdot Al_2O_3$ which is also isometric (Brownmiller, 1935), and apparently isostructural with $K_2O \cdot MgO \cdot SiO_2$.

$K_2O \cdot MgO \cdot SiO_2$ forms binary systems with $K_2O \cdot SiO_2$, $K_2O \cdot 2SiO_2$, $K_2O \cdot MgO \cdot 3SiO_2$, and probably with MgO (see figs. 5 and 6). The system with forsterite is only partially binary, as the field of periclase covers most of it.

*$K_2O \cdot MgO \cdot 3SiO_2$.*—The field of this compound is outlined on figure 5 by the line *I'Z B'F'G''G'I'*. The compound melts congruently and sharply to a rather thin liquid at 1134° ± 1°, which crystallizes readily upon cooling (within several minutes) to a granular mass. Very slow cooling of a liquid of this composition through the liquidus temperature yields large, sharp hexagonal tablets, uniaxial negative, with $n_\omega = 1.530 \pm .002$, $n_\epsilon = 1.524 \pm .002$ ($Na_D^{26°}$). In batches of other compositions and less often in the pure material, it crystallizes occasionally as trillings with hexagonal outline or fourlings with a rectangular or circular outline, but these twin crystals appeared to be almost optically continuous across the "twinning planes." In some cases a series of grooves were seen on the (0001) face of the hexagonal tablets, perpendicular to each edge exactly as in the pseudo-hexagonal cyclic twins of aragonite, but such crystals gave sharp, definitely uniaxial interference figures and uniform extinction throughout. Several runs yielded long, rectangular cross-section crystals of the compound with a twinning plane running the length of the crystal, the two halves showing 27° extinction against this plane. All of the above types of crystals are presumed to be the same phase and are here called $\alpha K_2O \cdot MgO \cdot 3SiO_2$. This is the form which occurred in those quenching runs where sufficiently large crystals were obtained to differentiate, but usually this was not possible. The compound has a definite inversion to a finely fibrous appearing, spherulitic form having an "extinction cross" parallel to the vibration directions of the nichols, usually with the fast ray parallel to the radius of the spherulite, although the reverse was found. The gross index of refraction of this material lies between the two indices of the other form (*i.e.*, approximately 1.527), and there appears to be a fairly large dispersion, but further data on the optical properties could not be obtained from these samples. As this form is apparently the stable one, it is called "$\beta K_2O \cdot MgO \cdot 3SiO_2$" here. The differences between the two forms under the microscope are not great, particularly in fine materials, and hence the inversion was not found until X-ray patterns were obtained. The nature of this inversion is unknown, as no quenching data could be found to indicate it, and high sensitivity differential thermal analysis run on a preparation consisting of the $\beta$ form showed no thermal activity from 20° to 1080°.

The hexagonal crystals seem to form first in any crystallization, and later slowly invert to the other form, even at temperatures just below the melting point. Optically the change seems to be gradual, but one series of X-ray patterns showed a rather abrupt change between samples held for 2 and 3 days at 1100°. Density measurements were not made of the $\alpha$ form, but there appears to be a volume change upon inversion. For additional data on this compound see "X-ray Data" section.

The compound $K_2O \cdot MgO \cdot 3SiO_2$ forms binary systems with the compounds $K_2O \cdot MgO \cdot SiO_2$(?), $K_2O \cdot 2SiO_2$, $K_2O \cdot MgO \cdot 5SiO_2$, and forsterite, as shown in figure 6. Glass of the composition $K_2O \cdot MgO \cdot 3SiO_2$ has a density of 2.40 and an index of 1.510, and crystals of the $\beta$ form have a density of 2.56.

*$K_2O \cdot MgO \cdot 5SiO_2$.*—The field of this compound is outlined by the line A′ZXVPQRC′B′A′ on figure 5. This compound melts congruently and sharply, though slowly, to a viscous liquid at 1089° ± 1°, and will start to crystallize from a melt of its own composition within a few hours at optimum temperatures. It occurs in two modifications; an isotropic form called "$\alpha$ $K_2O \cdot MgO \cdot 5SiO_2$," as tetrahexahedra and occasional octahedra and cubes with an index of 1.501 ± .002 ($Na_D^{32°}$); and a very weakly birefringent (estimated birefringence 0.001-0.002) spherulitic, almost fibrous form called "$\beta$ $K_2O \cdot MgO \cdot 5SiO_2$," showing wavy, irregular extinction, and an index of 1.505 ± .002 ($Na_D^{32°}$). The isotropic $\alpha$ form always seems to crystallize first, and, if sufficient time is allowed in the furnace, it slowly inverts to the anisotropic $\beta$ form, regardless of the temperature. The isotropic form has not been obtained free from both glass and the anisotropic form; whether this is due to the necessity of having glass present to prevent a "snap" inversion to the anisotropic form on cooling, or whether it is merely a result of inversion proceeding almost as fast as the crystallization of the isotropic form, is not known. It is very apparent, however, that the glass surrounding crystals of the isotropic form, and even that around those crystals that have inverted to the anisotropic one, is under strain indicating compression along the tangent and tension along the radius from each grain. This might be due to a shrinkage of the crystal upon inversion as would be indicated by the increase in index, but this would not explain similar strains around each seemingly perfectly isotropic crystal unless there is a

partial inversion that is not visible. Possibly these strains are attributable merely to large differences between the thermal expansions of the crystalline material and the glass. The strains in the glass frequently made it impossible to distinguish the two forms in the quenching runs, but in general the anisotropic $\beta$ form seemed far more common, the occurrence of the isotropic form being irregular. The inversion with time can be followed easily by X-ray methods (see beyond), but high sensitivity differential thermal analysis of a preparation consisting of the $\beta$ form showed no thermal activity from 20° to 1080°.

$K_2O \cdot MgO \cdot 5SiO_2$ forms binary systems with the compounds $K_2O \cdot MgO \cdot 3SiO_2$, $K_2O \cdot 4SiO_2$, $SiO_2$, and forsterite, and partially binary systems with $K_2O \cdot 2SiO_2$ and $K_2O \cdot 5MgO \cdot 12SiO_2$, as indicated in figure 6. Glass of the composition $K_2O \cdot MgO \cdot 5SiO_2$ has a density of 2.38 and an index of 1.498, and crystals of the $\beta$ form have a density of $2.39_5$.

*$K_2O \cdot 5MgO \cdot 12SiO_2$.*—This is the most interesting of the new ternary compounds, and was the most difficult to prove as to composition because of its incongruent melting and very small field on the liquidus surface (see fig. 5, area *TOPVXUT*). Although the field is small, it forms as one of the stable phases in all compositions in the triangle *LWS'* (figs. 5 and 8), and occasionally is formed metastably in compositions outside of that triangle. It generally crystallizes within a few days to sharp, thin, hexagonal tablets, frequently with the second-order prism and first- and second-order pyramids as modifying forms. The small crystals obtained here have no visible cleavage. Optically it is uniaxial positive, $n_o = 1.543$, $n_e = 1.550 \pm .002$ ($Na_D^{30°}$), $n_o - n_e = 0.008 \pm .002$. It should be noted that these optical properties are very similar to those of quartz. Crystals of the compound containing small amounts of glass and clinoenstatite (see beyond) had a density of 2.58.

The thermal behavior of this compound is illustrated by figure 7. Upon heating the pure crystals, they melt incongruently at 1174° ± 2° to form clinoenstatite (31.3 per cent) and liquid *T* (68.7 per cent). Above 1174° this clinoenstatite goes into solution, but at 1398° the liquid composition touches the forsterite-clinoenstatite reaction curve (*JU*, figs. 5 and 8) and thus the remaining clinoenstatite begins to break up to form forsterite and more liquid. At 1453° this reaction is

completed with the decomposition of the last trace of clinoenstatite; with further heating the remaining forsterite crystals start to dissolve and the liquid composition leaves the curve *JU* and approaches point *S*, where the last of the forsterite crystals dissolve at the forsterite liquidus temperature of 1467°.

As the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ is a little unusual, the following discussion is offered in its support. The best method of proving the composition of a compound in this type of work would be to synthesize an optically homogeneous crystalline phase of integral molecular ratio of constituents possessing the thermal behavior of a compound. From detailed work on the reaction curve *OTU* between the fields of clinoenstatite and $K_2O \cdot 5MgO \cdot 12SiO_2$ (see fig. 8), it was possible to locate the maximum point *T* with fair certainty although the temperature differences are small. On a theoretical basis the

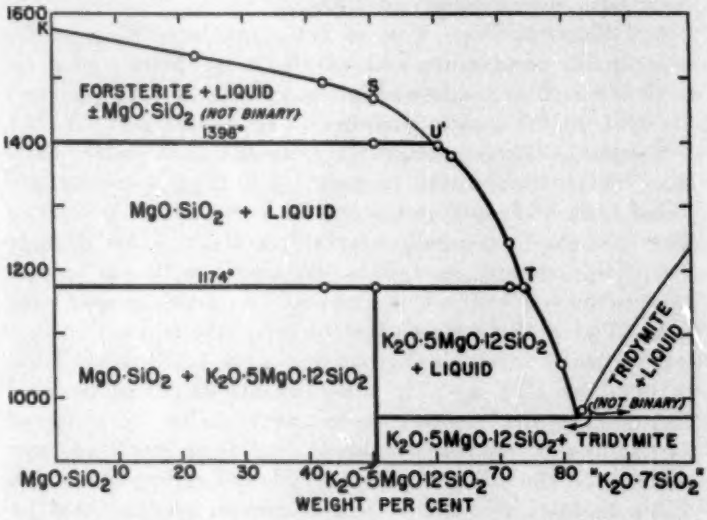


Fig. 7. Equilibrium diagram for the partially binary system $MgO \cdot SiO_2$-$K_2O \cdot 5MgO \cdot 12SiO_2$. This represents a cross section through the ternary system along the line KST (fig. 5), extended to its intersection with the $K_2O$-$SiO_2$ side at the molecular ratio $1K_2O:7SiO_2$ (not a compound). The letters used for the points are the same as those on figures 5 and 8. Heavy lines refer to binary equilibrium, light lines to non-binary (ternary) equilibrium. The small circles are experimentally determined points, mostly projected short distances (<0.5 per cent) along the isotherms in the ternary system.

composition of the (at that time) unknown phase would thus lie along the line connecting *T* with the composition of clinoenstatite (*K*). On the same basis the small maximum at *V* on the boundary curve *XVP* (between $K_2O \cdot MgO \cdot 5SiO_2$ and the unknown phase) would require that the composition of the unknown phase lie on the extension of the line *WV*. If the maxima *T* and *V* could be located with complete accuracy, this would be adequate to establish the composition of the phase, which must lie at the intersection of *WV* produced and *TK* in order to satisfy both requirements. Experimentally, however, this accuracy was not feasible. When the possible errors in location of *T* and *V* were taken into account a small area in the vicinity of point *S* was found to be the most likely. The only

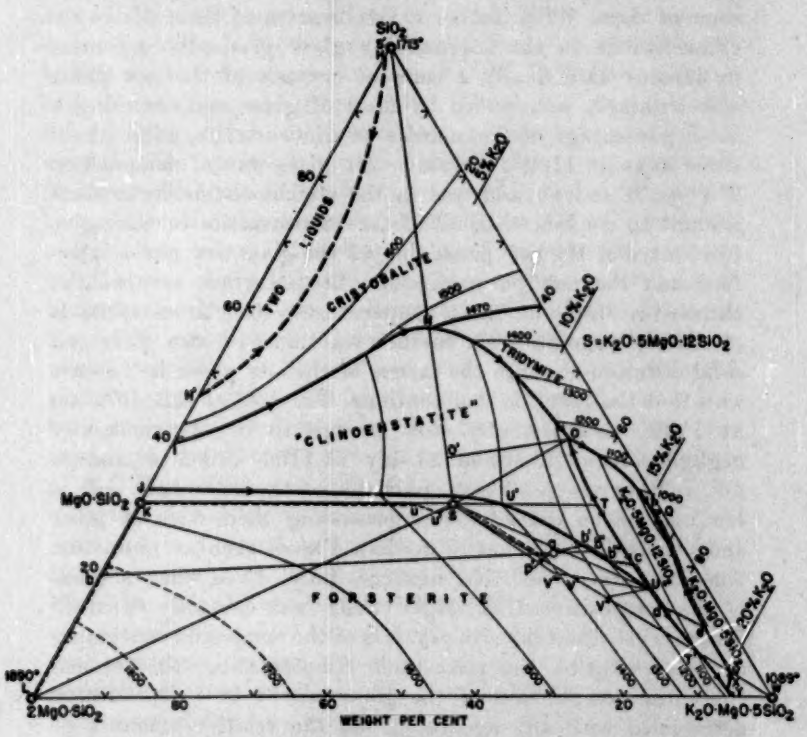


Fig. 8. Equilibrium diagram for the system Forsterite-$K_2O \cdot MgO \cdot 5SiO_2$-$SiO_2$. This represents a portion of the more general system $K_2O$-MgO-$SiO_2$ (the oblique triangle LWS' on figure 5). See text for description of crystallization paths.

integral molecular ratio that fell within this area that was at all rational was the composition $K_2O \cdot 5MgO \cdot 12SiO_2$.

The next step would be to produce a homogeneous crystalline product of this molecular ratio. A number of methods were tried unsuccessfully in an attempt to obtain such a product. When a glass of that composition (98 and 98a) was held at any temperature below the 1174° incongruent melting point, the first crystals to form were metastable "clinoenstatite" needles. This occurred within a few hours when held at 1100° and within a few days at temperatures around 875°. Within a day (or more at the lower temperatures) large hexagonal plates of the new compound started to grow in the glass surrounding the clinoenstatite needles and to enclose some of them. With further crystallization of these plates the clinoenstatite in the surrounding glass gradually decreased in amount until finally a mass of crystals of the new phase was obtained, surrounded by films of glass and enclosing a small precentage of fine needles of clinoenstatite, after about three days at 1100°. Actually this glass was of composition *T* (figs. 5 and 8) and was in the stoichiometrically correct amount to combine with all of the clinoenstatite remaining to form more of the new phase, but as the glass-new phase interface and the new phase-clinoenstatite interface are each in themselves stable at these temperatures, the clinoenstatite is effectively removed from further reaction with the glass and solid diffusion through the lattice of the new phase is the only way that the reaction can continue. The rate of this diffusion at 1100° is apparently slow enough to be experimentally negligible, as an additional 17 days at 1100° failed to produce any further visible change, particles of the new phase only a few microns in diameter still possessing their films of glass and enclosed clinoenstatite needles. Fluxes such as potassium tungstate were tried, but unsuccessfully. Even when a glass of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ was carefully "seeded" before crystallization with crystals of the compound containing no clinoenstatite, the metastable clinoenstatite still formed. Since the composition of the glass cannot be independently determined with any accuracy, and the relative amounts of glass and metastable clinoenstatite cannot be measured with any certainty in material of this type, the composition of the compound has not been proven by these data.

In order to prevent this formation of metastable clinoenstatite, crystallization of glasses of the composition $K_2O \cdot 5MgO \cdot 12SiO_2$ (98 and 98a) was attempted at 500° for 14 hours under a pressure of 6000 psi water in a bomb of the Morey type (Morey and Ingerson, 1937). The result was a mixture of two phases, containing approximately 10 per cent of large crystals of a hydrous prismatic material, and 90 per cent of a hydrous, fibrous, highly birefringent material with indices approximately 1.565 and 1.585. Both of these decomposed to an isotropic, low index material on being heated to 950° for three minutes. When this heated material was held in air at 1100° for one day, it yielded a mass of metastable clinoenstatite needles in glass.

As higher temperatures tend to prevent the formation of hydrous phases in bomb runs, samples were run at 900° and 15,000 psi water pressure for 1 hour in O. F. Tuttle's (1948) hydrothermal quenching apparatus. These runs were successful, yielding a product which was a mass of interlocking crystals with optical properties and X-ray powder patterns identical with those of the crystals formed in the "dry" manner but without the clinoenstatite. A small fraction of 1 per cent of some low index, extraneous material was present, presumably because slight impurities in the starting material (particularly the MgO) caused divergence of the batch from the theoretical composition. If the actual composition of the compound were such that it differed from 98 in having only 0.5 per cent more MgO, the crystalline material obtained here from 98 should contain only 94.5 per cent crystals of the compound, the other 5.5 per cent being either glass or crystals of $K_2O \cdot MgO \cdot 5SiO_2$ and $SiO_2$. This amount of such low index materials should be visible readily under the microscope when immersed in a liquid having the mean index of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals; if the compound contained 0.5 per cent less MgO than 98, the crystalline material obtained should consist of approximately 97.5 per cent of the compound and 2.5 per cent clinoenstatite, and the latter should be even more visible under the microscope as a result of its high index. Furthermore, even these differences in composition from that of 98 would not be sufficient to yield any rational formulas for the composition of the compound. The closest integral ratio of any simplicity and probability according to present knowledge of

silicate structure[32] is $K_2O \cdot 4MgO \cdot 10SiO_2$, but this composition is so far removed from 98 (it would have 11.0 per cent $K_2O$, 18.8 per cent MgO, and 70.2 per cent $SiO_2$) that, although the quenching data might possibly be interpreted in this light, the crystallization of 98 to a homogeneous crystalline phase prohibits it.

In order to prove that there was not a range of compositions that would have behavior similar to that of 98 upon crystallization, two other batches were given the same treatment at 900° and 15,000 psi water pressure. They were 17 (approximately 3.2 per cent more MgO) and 134 (approximately 3.8 per cent less MgO). The former yielded a mass of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals containing a mat of tiny clinoenstatite needles (theoretically 16 per cent by weight), and the latter a mass of $K_2O \cdot 5MgO \cdot 12SiO_2$ crystals coated with films of a low index material, presumably $K_2O \cdot MgO \cdot 5SiO_2$ and $SiO_2$ or glass.[33] The above data are considered adequate to establish with fair certainty that $K_2O \cdot 5MgO \cdot 12SiO_2$ is the composition of the compound. It is stable in equilibrium with $K_2O \cdot MgO \cdot 5SiO_2$, forsterite, clinoenstatite, and silica, although most of these sub-systems are not binary at liquidus temperatures due to the incongruent melting of the compound.

[32] *E.g.*, see Hendricks (1944). A series of infinite sheets of $(Si_4O_{10})_n^{-4n}$ as in the micas, bonded with K and Mg, would satisfy either $K_2O \cdot 4MgO \cdot 10SiO_2$ or $K_2O \cdot 5MgO \cdot 12SiO_2$, but layers of 12 coordination $K^+$ cannot exist as they do in the micas, as the crushed crystals showed no sign of the perfect cleavage of the micas.

[33] X-ray examination of these examples was not very satisfactory due to the overlap of strong $K_2O \cdot 5MgO \cdot 12SiO_2$ lines upon weak clinoenstatite and $K_2O \cdot MgO \cdot 5SiO_2$ lines.

(*To be continued*)

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# EXPERIMENTS ON THE MOVEMENT OF SHELLS BY WATER[1]

HENRY W. MENARD AND A. J. BOUCOT

ABSTRACT. Experiments in a laboratory flume indicate that the current velocity necessary to move terebratuloid brachiopod shells is only about one tenth of the velocity required to move pebbles of the same size. Movement of shells is controlled primarily by the relative ease of movement of the subjacent bed material; a shell may move over a bed of gravel but sink into a bed of sand because of the rapid removal of adjacent sand grains by scouring.

Shape, size, effective density, and ornamentation influence the competent velocity of a shell. Competent velocity increases with sphericity.

## INTRODUCTION

PALEOECOLOGISTS are aware that a fossil assemblage of shells does not necessarily represent a community assemblage preserved in place. Instead, the fossil assemblage may constitute a diverse assortment of shells brought together by physical agencies, ordinarily after death, and then buried. Moving water is one of the most important agents affecting the transportation and sorting of unattached dead shells or those otherwise incapable of independent movement. The writers know of no experimental observations on the current velocities required to initiate the movement of shells, nor of the effect of transportation on an assemblage. For these reasons it seemed desirable to make such observations when a hydraulic flume temporarily became available at the Woods Hole Oceanographic Institution in the fall of 1948.

During the experiments, the relations between the variables affecting the movement of the shells seemed to be simple; so no exhaustive study was attempted. Subsequent analysis of the observations revealed that the relations were unexpectedly complex. It is apparent now that many more experiments will be required before the initial movement of shells can be explained completely or predicted. Consequently, the present conclusions cannot be offered as more than first approximations. They are submitted at this time because neither of the writers is likely to have access to a hydraulic flume in the near future.

This paper presents some results of the tests, as well as a brief consideration of their significance with regard to paleoecology. The writers wish to express their appreciation to

[1] Contribution No. 546 from the Woods Hole Oceanographic Institution.

P. E. Cloud, W. C. Krumbein, Henry C. Stetson, Fred B. Phleger and J. Wyatt Durham for reading the manuscript and offering suggestions for its improvement. Dr. Cloud initiated the statistical analysis of the data. In this analysis he was advised by F. M. Wadley; W. Peddle made most of these computations. The writers are also indebted to the Woods Hole Oceanographic Institution for the use of laboratory facilities, particularly the flume.

The experiments were done in a wooden flume one foot wide and 6 feet long, with a glass observation panel in one side. In 26 tests, a recess in the central 3 feet of the flume was filled with medium-fine sand (diameter 0.36 mm.) to the level of the flume bottom; in one test, the recess was filled with a gravel composed of grains 2-5 mm. in diameter. The bottom of the flume had a fixed slope of 0.002 during all these tests. In a typical run, a tailgate was fixed in place in order to produce the desired depth of flow in the flume; several shells were placed on the smoothed sand bottom; and the flume was filled with fresh water at a rate slow enough so that neither the shells nor the sand were disturbed; then the flow of water in the flume gradually was increased until one of the shells or the sand moved. The depth of water in the flume and the discharge of the water were measured when movement occurred. The mean current velocity was then calculated by dividing the discharge by the cross-sectional area of the flow within the flume.

Some 27 runs were executed, and 39 individual dry shells, representing 9 species of terebratuloid brachiopods, were tested. Observations were made on the current velocity competent to move the shells, the nature of the movement, scour of sand around the shells, and the orientation of the shells during and after movement. The length, width, thickness, weight, nominal diameter, and sphericity of the shells used in these runs, and the results of the tests are shown in tables 1 and 2.

The velocity required to move a brachiopod shell lying free on a substratum of sand depends on the shell properties of size, effective density, shape, and ornamentation, and on whether the valves are hinged together or separated. All these variables except ornamentation are considered in the present tests. The most important variable governing the initial movement of shells, however, appears to be the relative ease of

movement of the shell and the underlying sand grains. Thus, a certain current may roll a shell over a gravel bottom with ease, but be incapable of moving it over sand because the sand moves more readily than the shell. If the sand moves first, a scour is formed around the shell, which may be dropped into it and buried by moving sand. Because of the importance of the relative ease of motion of sand and shells, the detailed discussion of the tests is divided into two sections, one concerned with shells which move more easily than sand, and the other concerned with shells which move less easily than sand.

### WHOLE SHELLS WHICH ARE EASIER TO MOVE THAN THE UNDERLYING SAND

Unattached shells are clastic particles in the same sense as grains of sand or gravel, and hence the factors governing their movement are the same. As the movement of sand and gravel has been studied in great detail whereas the movement of shells has not, it seems profitable to consider sediment movement before turning to shell movement.

The characteristics of a grain which influence its initial movement on the bed of a watercourse are the size, density, and shape. Hydraulic engineers generally agree that the current velocity competent to move coarse sand and pebbles is proportional to the square root of the diameter of the grains (Hjulstrom, 1935); the same proportionality probably holds for all larger sizes of gravel (Menard, 1949). The competent velocity commonly is thought to be proportional to the square root of the effective density (weight per unit volume if the grains are immersed in water). As to the shape, Krumbein (1942) finds that the more spherical a grain of gravel, the slower the current required to put it in motion.

The present tests show that the initial movement of terebratuloid brachiopods depends primarily on the effective density because that variable appears to govern whether a shell moves more easily than the sand on which it rests. Secondarily, the velocity required to initiate motion appears to depend on the shape and size of the shell. Although the movement of shells and of gravel and sand is necessarily controlled by the same physical characteristics, it is apparent that the relative importance of these characteristics varies.

EFFECTIVE DENSITY

All the whole *Terebratulina* shells tested were moved by currents which were incapable of moving the bed of sand, although the shells weighed as much as 0.605 gram and the sand grains weighed only a few thousandths of a gram. This seeming paradox is due to the very small density of the shell and its contained water as compared to the solid quartz grains. If shell number 4, for example, is filled with water, the shell-water combination has a density in air of 1.28 gms./cc.; however, if the combination is under water, the buoyancy of the displaced water reduces the effective density to 0.28 gm./cc. A water-filled shell moved by a slow current is analogous to an inflated balloon moved by the faintest breeze although the rubber in the balloon weighs several grams.

Species and individuals differ in effective density, and, therefore, in competent velocity. Hence moving water may tend to sort a mixture of individuals of two species into groups according to species—rather than size or shape—if the effective densities of the two species are very different and the range in size and shape is small. Some effective density determinations for terebratuloid brachiopods appear in table 1.[1] The values show that the effective density of *Terebratulina septentrionalis* ranges from 0.28 to 0.43 gm./cc., and that it decreases as the size increases. The effective density of *Terebratalia transversa* ranges from 0.35 to 0.42 but does not vary systematically with size.

Studies of sediment movement indicate that competent velocity is proportional to the square root of effective density. Applying this proportion to brachiopod shells suggests that the competent velocity of a one-centimeter *T. transversa* shell is only slightly larger than that of a *T. septentrionalis* shell of about the same size and shape.

SIZE

The size of irregularly shaped shells may be expressed in terms of a nominal diameter equal to that of a sphere of the

[1] A dry shell was weighed in air, and the approximate volume was determined by dividing the weight by the density of calcite (2.72 gms./cc.). The shell was then filled with water and weighed. The weight of the dry shell was substracted from the weight of the water-filled shell in order to obtain the weight of the water, and thereby its volume. The density of the water-filled shell was calculated by dividing the sum of the volume of the shell and of the contained water by the total weight.

same volume. For the present purposes, a nominal diameter has been determined by taking the cube root of the product of the length, width, and thickness of each shell. Thirty-one shells (including single pedicle and brachial valves as well as whole shells) with nominal diameters ranging from 0.41 to 5.50 millimeters were moved while resting on a substratum of either medium-fine sand or gravel. The current velocity required to initiate the motion of each of the shells is shown in graphic form in figure 1, in which the competent velocity in centimeters per second is plotted against the nominal diameter in centimeters. The graph paper is logarithmic because experiments with sediments have shown that functions of these two variables yield a straight line on logarithmic paper. This relation provides an easy means of establishing whether or not the initial movement of shells is controlled by the size of the shells in the same way that the initial movement of sediment is controlled by the size of the grains.

The points relating competent velocity and nominal diameter in figure 1 are scattered, but the area in which the points lie has a trend which suggests that the velocity is proportional to the square root of the diameter, as it is for sand and gravel. The coefficient of correlation for a least squares regression line based on all the data in which the bed was sand gives a low positive correlation of 0.585.[2] If the data for a gravel bed are included, a high positive correlation of 0.820[2] is indicated. However, combining data from different experimental conditions introduces some bias into the calculations. The scattering of points indicates that the nominal diameter of a shell is not the only variable affecting its competent velocity. This indication agrees with the general body of hydrodynamical theory and observation. Rouse (1938, p. 216) says that if the wake behind an object is completely turbulent, the drag exerted upon the object by a moving fluid is almost completely independent of the Reynolds number (a criterion of turbulence). The Reynolds number in the present experiments is the product of the current velocity and the nominal diameter divided by the kinematic viscosity; the value of the Reynolds number is great enough to establish that the wake was always turbulent. With regard to shells (nominal diameter larger than about one centimeter), therefore, Rouse's statement indicates that

[2] Computed by W. Peddle.

TABLE 1

Physical Characteristics and Flume Behavior of Terebratuloid Brachiopod Shells Resting on a Bed of Sand or Gravel

| No. | Species | Type of Shell | Length (cm.) | Width (cm.) | Thickness (cm.) | Weight (gms.) | Sphericity | Nominal Diameter (cm.) | Effective Density (gm./cc.) | Medium Sand Bed: Competent Velocity (cm./sec.) | Medium Sand Bed: Current Velocity At Which Specimens First Turned Over (cm./sec.): Single Valve Concave Upward or Whole Shell | Medium Sand Bed: Current Velocity At Which Specimens First Turned Over (cm./sec.): Single Valve Convex Upward | Gravel Bed: Competent Velocity (cm./sec.) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | *Terebratulina septentrionalis* | Whole | 2.41 | 1.99 | 1.21 | 0.790 | 0.745 | 1.80 | | | | | |
| 2 | | Whole | 2.09 | 1.74 | 1.20 | 0.605 | | | | | | | |
| 3 | | Whole | 1.82 | 1.40 | 0.81 | 0.365 | .700 | 1.27 | | 13.8 | 13.8 | | |
| 4 | | Whole | 1.70 | 1.36 | 0.82 | 0.325 | .728 | 1.24 | 0.28 | 13.3 | 13.3 | | |
| 5 | | Whole | 1.63 | 1.17 | 0.74 | 0.230 | .688 | 1.12 | (0.30) | 13.8 | 13.8 | | |
| 6 | | Whole | 1.32 | 1.10 | 0.65 | 0.165 | .744 | .98 | 0.32 | 15.1 | 15.1 | | |
| 7 | | Whole | 1.21 | 0.83 | 0.57 | 0.135 | .687 | .83 | (0.36) | 11.7 | 11.7 | | |
| 8 | | Whole | 0.98 | 0.75 | 0.44 | 0.085 | .701 | .69 | 0.43 | 15.1 | 15.1 | | |
| 9 | | Whole | 0.76 | 0.57 | 0.36 | 0.050 | .708 | .54 | | 11.7 | 11.7 | | |
| 10 | | Whole | 0.62 | 0.46 | 0.38 | 0.035 | .769 | .48 | | 11.7 | 11.7 | | |
| 11 | | Whole | 0.62 | 0.44 | 0.26 | 0.020 | .667 | .41 | | 12.1 | 12.1 | | |
| 12 | | Pedicle valve | 2.29 | 1.60 | 0.69 | 0.407 | .595 | 1.36 | | 11.1 | 12.0 | 14.9 | |
| 13 | | Pedicle valve | 1.92 | 1.49 | 0.51 | 0.307 | .591 | 1.13 | | 11.1 | | | |
| 14 | | Pedicle valve | 1.81 | 1.34 | 0.48 | 0.225 | .582 | 1.05 | | 10.1 | 10.1 | 14.7 | |
| 15 | | Pedicle valve | 1.61 | 1.11 | 0.43 | 0.115 | .569 | .92 | | 10.1 | 10.1 | 14.9 | |
| 16 | | Pedicle valve | 1.19 | 0.85 | 0.28 | 0.055 | .551 | .66 | | 10.1 | 11.1<br>10.6 | 14.9 | |
| 17 | | Brachial valve | 1.65 | 1.47 | 0.40 | 0.217 | .600 | .99 | | 9.4 | | SMF* | |
| 18 | | Brachial valve | 1.57 | 1.31 | 0.51 | 0.257 | .647 | 1.02 | | 11.6 | 11.6 | SMF* | |
| 19 | | Brachial valve | 1.50 | 1.35 | 0.34 | 0.135 | .589 | .88 | | 9.4 | 10.6 | SMF* | |
| 20 | | Brachial valve | 1.35 | 1.02 | 0.37 | 0.112 | .592 | .80 | | 10.6 | 10.6 | 14.4 | |

TABLE 1 (*Continued*)

| No. | Species | Type of Shell | Length (cm.) | Width (cm.) | Thickness (cm.) | Weight (gms.) | Sphericity | Nominal Diameter (cm.) | Effective Density (gm./cc.) | Medium Sand Bed: Competent Velocity (cm./sec.) | Medium Sand Bed: Current Velocity At Which Specimens First Turned Over (cm./sec.): Single Valve Concave Upward or Whole Shell | Medium Sand Bed: Current Velocity At Which Specimens First Turned Over (cm./sec.): Single Valve Convex Upward | Gravel Bed: Competent Velocity (cm./sec.) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | *Terebratulina* | Brachial valves | 1.45 | 1.13 | 0.38 | 0.102 | .590 | .85 | | 9.4 | 10.6 | SMF* | |
| 22 | *septentrionalis* | | 1.04 | 0.85 | 0.18 | 0.042 | .522 | .54 | | 8.6 | 9.4 | SMF* | |
| 23 | *Terebratalia transversa* (Sowerby) | Whole | 1.41 | 1.61 | 0.68 | 0.255 | .718 | 1.15 | 0.35 | 15.0 | 15.0 | SMF* | |
| 24 | | Whole | 2.19 | 2.63 | 1.19 | 1.763 | .721 | 1.90 | 0.42 | SMF* | | | |
| 25 | | Whole | 2.74 | 3.22 | 1.46 | 3.036 | .728 | 2.34 | 0.39 | SMF* | | | SMF* |
| 26 | | Whole | 3.07 | 3.89 | 1.83 | 5.337 | .719 | 2.80 | 0.41 | SMF* | | | |
| 27 | | Whole | 4.00 | 4.28 | 2.53 | 10.384 | .820 | 3.52 | 0.37 | SMF* | | | |
| 28 | | Whole | 3.55 | 4.53 | 2.30 | 9.400 | .745 | 3.38 | | SMF* | | | SMF* |
| 29 | *Magellania flavescens* | Whole | 2.95 | 2.35 | 1.63 | 2.496 | .761 | 2.24 | | 17.6 | 17.6 | | |
| 30 | *Terebratalia rubescens* | Whole | 1.94 | 2.72 | 1.15 | 1.467 | .639 | 1.82 | | SMF* | | | |
| 31 | *Neothyris venosa* (Solander) | Whole | 6.95 | 6.33 | 3.78 | 18.677 | .791 | 5.50 | | SMF* | | | 26.8 |
| 32 | *Laqueus californicus* | Pedicle valve | 3.55 | 3.90 | 1.15 | 5.445 | .694 | 2.52 | | SMF* | | | |
| 33 | | Brachial valve | 3.60 | 4.22 | 1.15 | 2.65 | .679 | 2.60 | | 17.6 | 17.6 | | |
| 34 | *Terebratulina caput-serpentis* (Linné) | Whole | 1.96 | 1.65 | 0.86 | 0.410 | .718 | 1.41 | | 17.6 | | | |
| 35 | *Waldheimia florida* (Portales) | Pedicle valve | 2.05 | 2.23 | 0.94 | 0.295 | .650 | 1.63 | | 12.6 | | | |
| 36 | | Brachial valve | 1.75 | 2.23 | 0.59 | 0.214 | .528 | 1.32 | | 14.8 | 14.8 | 16.7 | |
| 37 | | Whole | 2.17 | 2.28 | 1.50 | 0.703 | .770 | 1.95 | | 12.6 | 12.6 | | |
| 38 | *Laqueus californicus* | Whole | 2.79 | 2.44 | 1.45 | 0.675 | .770 | 2.14 | | 12.6 | 12.6 | | |
| 39 | *Terebratella dorsata* (Gmelin) | Whole | 3.48 | 3.63 | 2.08 | 4.751 | .859 | 2.98 | | SMF* | | | 26.8 |

* Sand Moved First.

( ) Parentheses indicate interpolated values.

the current velocity necessary to initiate motion may even be independent of the size.

### SHAPE

The shape of shells may be expressed in terms of *true sphericity*—the surface area of a sphere divided by the surface area of a shell of the same volume (Wadell, 1932). Because the surface area of a shell is difficult to measure, the shape is here expressed in terms of ratios of diameters—the *intercept sphericity* of Krumbein (1941). Intercept sphericity is equal to the cube root of the following quantity: the intermediate diameter times the smallest diameter divided by the square of the largest diameter. This is an approximation of sphericity as defined by Wadell. In the present tests, the thickness is always the small diameter, but either the width or length may be the intermediate or large diameter. Sphericity for the 31 shells which were moved had a range of 0.522 to 0.859.

It will be shown in the following paragraphs that there is a correlation between the intercept sphericity of a shell and the

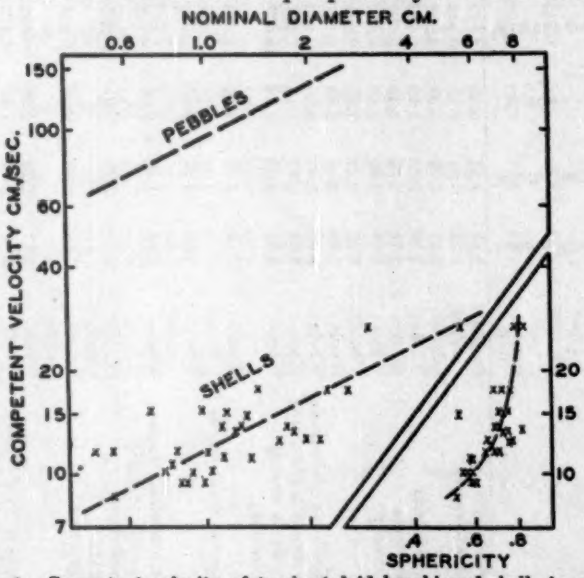



Fig. 1. Competent velocity of terebratuloid brachiopod shells in relation to nominal diameter and sphericity. The competent velocity of pebbles is shown for comparison.

current velocity required to put it in motion. The correlation appears to indicate that intercept sphericity is an index of the shape of terebratuloid brachiopod shells; but the correlation does not mean that the intercept sphericity represents a complete expression of the shape of the shells. Intercept sphericity represents an approximation of true sphericity which holds because of the general resemblance between pebbles and a triaxial ellipsoid. If the intercept sphericity is a valid expression for the shape of only those shells which resemble triaxial ellipsoids, it will prove of little value in measuring the shape of most shells which, unlike terebratuloid brachiopods, are irregular. It is interesting to note, however, that in the present experiments with single valves the intercept sphericity appears to give a more accurate expression of shell shape than does the true sphericity. True sphericity appears to have little significance as a measure of the shape of single valves because each valve is essentially a curved plate, and this sphericity takes no account of the curvature of such a plate.

Engineers divide the total drag exerted on an object by a moving fluid into two parts: "surface drag" resulting from the retardation of the fluid at the solid boundary, and "form drag" resulting in large part from the pull exerted by the low pressure area in the wake of the particle. Neither true sphericity nor intercept sphericity is an exact expression for the sum of surface and form drag; hence neither is capable of measuring the total effect of shape upon the hydraulic behavior of a particle. True sphericity appears to be an index of surface drag but it takes little account of form drag. Consequently it gives an indication of the hydraulic behavior of particles of approximately the same shape, but not of particles with very different shapes, because the wakes are different. Intercept sphericity gives some measure of the surface drag of ellipsoidal particles and also of form drag, because it is based on ratios of diameters. With regard to hydraulic behavior, therefore, intercept sphericity may surpass true sphericity as an index of shape of sand and gravel particles. Irregular shapes such as shells are far more complex, and their hydraulic behavior will not be understood completely until the principles of fluid dynamics are applied to their study. Neither true nor intercept sphericity, for example, is capable of indicating any significant difference in the hydraulic behavior

of a rectangle and of an airfoil of about the same dimensions, although the form drag of the airfoil is much less than that of the rectangle, and the lift resulting from the shape of the airfoil might have a pronounced effect on its movement. A section of a pecten perpendicular to the hinge line resembles an airfoil, so it is doubtful if any type of sphericity would provide a significant index of its shape in relation to hydraulic behavior.

Figure 2 shows the sphericity of the various shells graphed against the current velocity required to put them in motion. For purposes of comparison, the figure also shows the effect of particle sphericity on the settling velocity and competent velocity of synthetic pebbles with a nominal diameter of about 14.5 mm. (Krumbein, 1942), and also on the settling velocity of molded lead particles (Wadell, 1934). The points relating sphericity and competent velocity of shells are scattered, and the trend of the relation is subject to several interpretations. The four most reasonable interpretations are shown in figure 3. In the first and second interpretations, the data for single valves and whole shells are combined; therefore the relation between sphericity and competent velocity is assumed to be continuous as shown by Wadell (1934). In the third and fourth interpretations, the data for single valves and whole shells are separated; therefore it is assumed that the relation is discontinuous (but continuous for various classes of shapes, such as rollers, disks, or spheriods) as shown by Krumbein (1942). In the first and third interpretations, the data for movement on a sand bed are combined with the data for movement on a gravel bed; in the second and fourth interpretations, these data are not combined. Statistically there is reason to separate the data concerning movement on two sizes of bed material because the experimental conditions were different; combining the data may bias any interpretation. Hydraulically the bias does not appear to be important. The change in bed type probably altered the boundary conditions of the flow in the flume; this probably altered the distribution of velocity in the main body of the flow but the average alteration probably was minor. The shells were all large compared to the thickness of any laminar boundary layer, and therefore most of the surface of shells on either the sand or gravel bed was exposed to the relatively undisturbed turbulent flow outside the boundary layer. The data are subject to too many interpretations to justify any more extensive discussion of this bias.

Despite their diversity, the interpretations indicate that there is some correlation between the sphericity of a shell and the current velocity required to move it. Some measure of the correlation can be determined by drawing a least square regression line for each interpretation, and calculating a coefficient of correlation for the deviation of the points from that line. Interpretation one (figure 3) gives a positive correlation of 0.699[8] for the straight line; no coefficient of correlation can be calculated for a curved line. "Positive" applied to a correlation

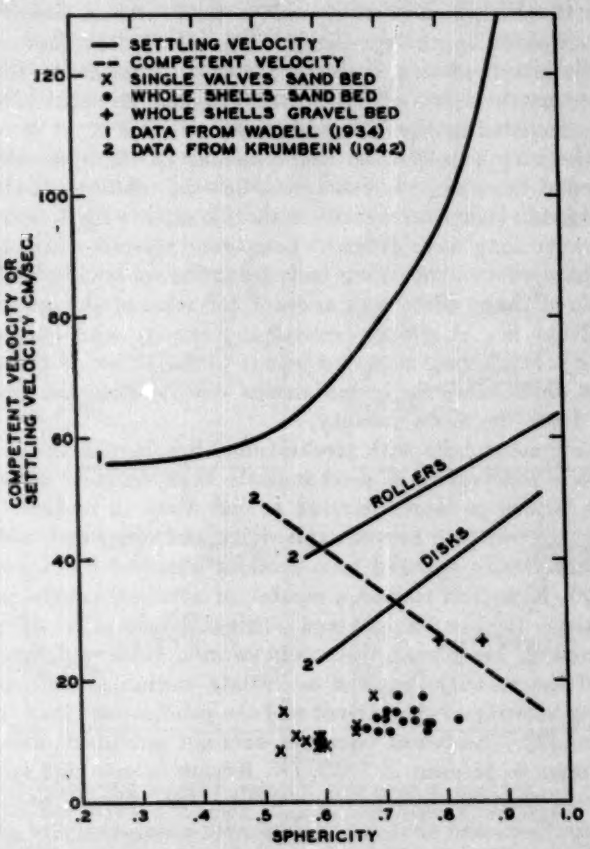



Fig. 2. Effect of sphericity upon the competent velocity and settling velocity of various kinds of particles.

[8] Computed by W. Peddle.

coefficient refers only to its algebraic sign. It is not an indication of certainty. Interpretation two gives a low positive correlation of 0.603 for whole shells.[4] Interpretation three gives a low positive correlation of 0.588. Interpretation four gives a positive correlation coefficient of 0.069 for whole shells, indicating no correlation; for all single valves together it gives a low positive correlation of 0.495; for single valves of one species, *Terebratulina septentrionalis*, it gives a positive correlation of 0.659. Thus almost all of the interpretations suggest that the competent velocity of a terebratuloid brachiopod shell depends on the sphericity of the shell; but part of the fourth interpretation indicates no such dependence for the limited number (16) of observations of the movement of whole shells included in the interpretation.

Sphericity is related to shape insofar as the hydraulic behavior of these shells is concerned, but the relation is only approximate. Hence two shells with the same weight, size and sphericity may have different competent velocities because of the shape effect which is not included in the sphericity. This unmeasured shape effect may account for some of the scattering of points in the graphs relating sphericity and competent velocity. Scattering may also be due to the action of turbulent eddies which cause the instantaneous velocity around a shell to vary from the mean velocity.

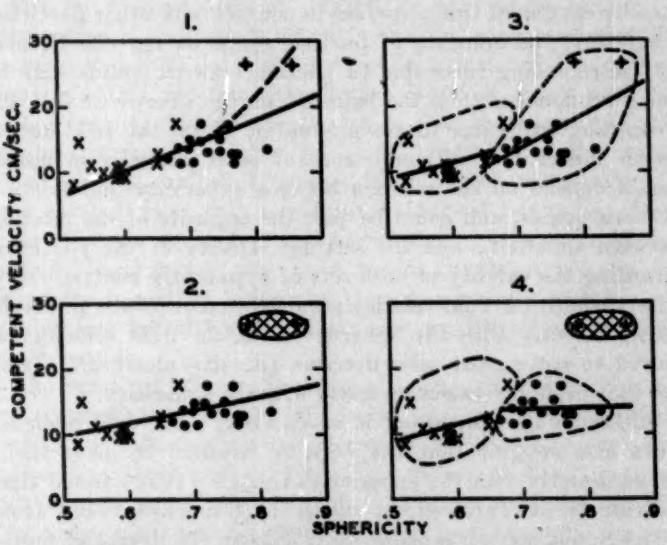
The present tests with terebratuloid brachiopod shells resting on a substratum of sand indicate that the more spherical shells require a faster current to put them in motion. This qualitative relation between sphericity and competent velocity is diametrically opposed to a relation observed by Krumbein (1942). Krumbein molded a number of artificial pebbles which had about the same weight and nominal diameter but different sphericities. He placed these pebbles in a flume and then observed the velocity required to initiate motion as well as the relative velocity of the current and the pebbles once they began to move. The competent velocities were not published; however, in a letter to Menard in 1949, Dr. Krumbein was kind enough to state that the competent velocity for spheres averaged 14.5 cm./sec., and that for pebbles with a sphericity of about 0.5 the competent velocity averaged 42.2 cm./sec. Thus the velocity required to initiate motion appeared to vary inversely

[4] Computed by W. Peddle.

with the sphericity. Computations by the present writers using Krumbein's published data on critical Froude numbers yield the competence-sphericity relation shown in figure 2.

On the other hand, Krumbein (1942) also measured the settling velocity of the artificial pebbles, and his figure 4 (p. 627) shows that the settling velocity varies directly with the sphericity. Wadell (1934) had noted a similar relation between settling velocity and sphericity. Both Krumbein's and Wadell's data are plotted in figure 2. The settling velocity of particles larger than a few millimeters in diameter is directly proportional to the competent velocity (Hjulstrom, 1935; Menard, 1949). Consequently, with regard to the relation between competent velocity and sphericity, Krumbein's tests with settling velocities agree with the flume tests of the present writers.

The contradictions in observations of the competence-sphericity relation of particles in flumes may be more apparent than real. A particle is put in motion in a flume if the propelling




1.&2. GROUPING SINGLE VALVES AND WHOLE SHELLS
3.&4. SEPARATING SINGLE VALVES AND WHOLE SHELLS
1.&3. INCLUDING DATA FOR GRAVEL BED
2.&4. EXCLUDING DATA FOR GRAVEL BED

Fig. 3. Possible interpretations of the effect of sphericity upon the competent velocity of terebratuloid brachiopod shells.

force due to moving water exceeds the retarding force due to friction between the particle and the adjacent particles of the bed. Particle shape may have some influence on the effectiveness of both the propelling and the retarding forces. Tentatively, the present writers believe that the differences in the observed influence of sphericity on competence may be ascribed to the differences in the effective density of the particles in the two experiments. The effective density of the shells is less than one-fifth of the effective density of Krumbein's synthetic pebbles. The shape of the shells may have more influence on the effectiveness of the drag due to the moving water than on the effectiveness of the friction between the shells and the sand bed. As a result the relation between sphericity and competence of shells in a flume corresponds to the relation between sphericity and settling velocity (in which there is no friction with adjacent particles). With denser particles, however, the proportion of the grain surface exposed to moving water is much smaller compared to the surface in contact with other particles. Therefore, the influence of particle shape on the effectiveness of the retarding force due to friction between grains may be more pronounced than the influence on the effectiveness of the propelling force due to moving water. If so, the relation between sphericity and competence of solid particles in flumes would depend on the relation between sphericity and friction between grains, and could be just the opposite of the relation between sphericity and the settling velocity of the particles. Granting the validity of both sets of apparently contradictory observations, the fluid velocity required to move shells probably varies directly with the sphericity, but the fluid velocity required to move most solid detritus (density about 2.7 grams per cc.) probably varies inversely with the sphericity.

Although the conclusion is speculative, some field observations also suggest that the velocity required to move shells varies directly with the sphericity. DuBois (1916) found that individuals of *Terebratalia obsoleta* (Sowerby) taken from Puget Sound varied in shape according to the degree of movement of the waters in which they lived. The more spherical shells were developed in the fastest currents. As the variation in shape represents an adaptation to differences in current velocity, the more spherical forms must be those which are best adapted to live where the currents are faster. The shape

may be related to some secondary characteristic of fast currents—such as an increased oxygen or food supply—but if the adaptation of shape is necessary in order to counterbalance the velocity of the water, a more spherical shape must be the one which is least affected by moving water. Therefore, the velocity necessary to initiate motion appears to vary directly with the sphericity.

### ORNAMENTATION

The effect of variations in ornamentation upon the movement of shells can not be evaluated from the present tests because all the shells are relatively smooth. Variations in ornamentation, however, are variations in shape, so it is apparent that they influence the relative ease with which a shell may be put in motion.

### HYDRAULIC FACTORS

The initial movement of a shell on the sandy bed of a watercourse is influenced not only by the characteristics of the sand and shell but also by the flow characteristics of the running water. Friction retards the layer of water next to the bottom and sides of the channel so that the velocity of the water on a sand bed may be only a fraction of the mean velocity of the current. However, the retarded or "boundary" layer rarely is more than a millimeter thick; all but the smallest shells protrude through it and are exposed to the force of the current. Medium and fine sand grains, however, usually lie within the boundary layer and thus may remain undisturbed on a stream bed although shells which are larger and heavier are in motion.

The measured effective densities of terebratuloid brachiopods are so small that the initial motion of any particular shell probably is influenced by the degree of turbulence of the moving water. Hjulstrom (1935) has shown that all natural watercourses are characterized by turbulent, eddying motion. The eddies may move in any direction relative to the general motion of the water, with the result that at any instant some parcels of water move faster than the average and some move slower. Due to the entirely random motion in a turbulent fluid, a comparatively rapidly moving eddy may strike a large shell and put it in motion although a smaller shell only a few centimeters away remains fixed in position because the force of the

water in that place is much smaller. The analogous effect of turbulence in air may be observed when a gust of wind swirls a patch of dust upward while the surrounding dust remains in place, or when a "cats-paw" ripples a water surface in some spots but leaves the remainder smooth. These commonplace phenomena indicate how turbulence may cause the larger of two shells of the same species to be moved instead of the smaller.

The quantitative importance of the turbulent eddies with regard to initiating motion in whole shells depends on the comparative velocity of the eddies and the current as a whole. This relation has been the subject of a great deal of study by hydraulic engineers, and it is known that the importance of the eddies increases with the cross-sectional area of the current if all other things are equal. In a small stream, for example, the eddy velocity might be only a fraction of the current velocity, but in a large slow current on a continental shelf the eddies might flow several times as fast as the average current velocity.

Perhaps the most significant conclusion to be derived from this analysis is that some terebratuloid brachiopod shells may be moved so readily that they are capable of being transported by the low current velocities now found on the continental shelves and slopes. All sizes of *Terebratulina septentrionalis* tested were moved by currents with velocities of 11.7 to 15.1 cm./sec.; Shepard (1948) has recorded bottom velocities of 36.7 cm./sec. in 160 fathoms on the California continental borderland, and 14.6 cm./sec. in 1050 fathoms in the Santa Cruz basin. These velocities were measured in the open ocean where tidal effects were negligible. However, in bays and estuaries where the tidal range is large, current velocities commonly are several times as great.

### WHOLE SHELLS WHICH ARE MORE DIFFICULT TO MOVE THAN THE UNDERLYING SAND

Flume tests with individuals of *Terebratalia transversa* show that the transportation of shells may depend on a critical relation between the competent velocity of the shells and of the sand in the bed. The smallest of five individuals resting on a bed of monodisperse sand grains with a median diameter of 0.36 mm., was moved by a velocity of 15.0 cm./sec. At the same time the sand was scoured from around the remaining four larger shells. A faster current caused the whole

surface of the bed to move although the shells remained fixed. They then began to settle into holes in the sand which were produced by the scour around them. This sequence of events is depicted in figure 4. Similar scour around pebbles was noted in earlier experiments in the flume, and fossil scour marks have been observed by Peabody (1947) in the Moencopi formation of the Grand Canyon area. If a current moves the subjacent sand instead of a shell the shell may become buried. However, this burial may depend on whether the sand is being eroded or

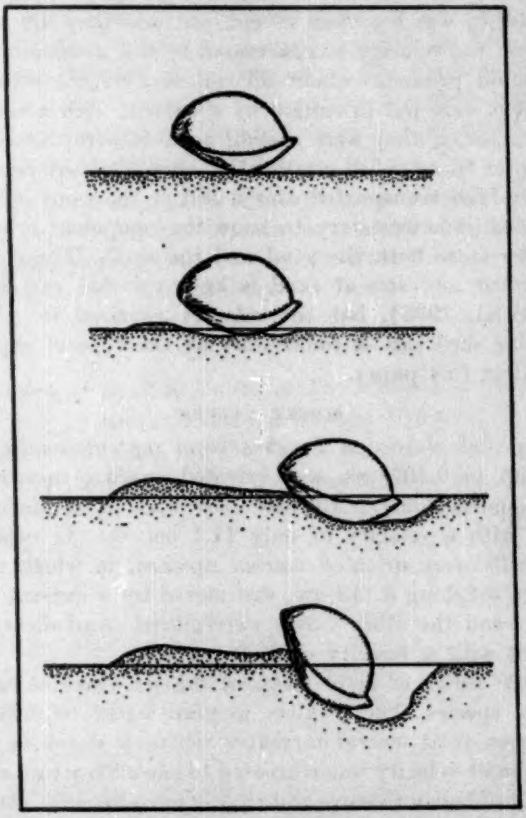


Fig. 4. A terebratuloid brachiopod (*Terebratulina septentrionalis*) being buried in sand because of scour by moving water. Four stages in the burial, of which the first is uppermost, are depicted in cross sections parallel to the direction of flow. In all the stages the water is moving from right to left, and at a constant velocity.

deposited; if erosion prevails, the shell remains exposed, whereas if deposition prevails, it is covered.

It follows that the size of the grains in the bed may determine whether a shell is moved by water with a given current velocity. A current which could move a shell on a bed of coarse sand might cause it to be buried in a finer sand, because the latter would be scoured from around the shell.

The effect of the size of particles in a substratum is shown by the tests with shells number 31 and 39. If these shells were resting on medium sand, they began to be buried when the current velocity was less than 20 cm./sec. and they did not move even when the velocity was increased to the maximum that the flume could produce—about 35 cm./sec. On the other hand, both shells were put in motion by a current with a velocity of 26.8 cm./sec. if they were resting on a substratum of gravel.

In order to establish whether an assemblage of fossil shells can have been transported over a bed of the sand in which it is enclosed, it is necessary to know the competent velocity required to move both the sand and the shells. The competent velocity for any size of sand is known within certain limits (Hjulstrom, 1935), but the velocity required to move any particular shell can be found only by the type of experiment reported in this paper.

### SINGLE VALVES

Five pedicle valves of *Terebratulina septentrionalis*, weighing 0.055 to 0.407 gm. and oriented concave upward, were tested simultaneously. All were moved small distances by a current with a velocity of only 11.1 cm./sec. In other tests these shells were oriented convex upward, in which position one valve weighing 0.115 gm. was moved by a current of 11.1 cm./sec., and the other valves were moved small distances by a current with a velocity of 14.9 cm./sec.

Another series of tests featured the six brachial valves of the same species. These valves weighed 0.042 to 0.257 gms. Their behavior at several current velocities is shown in table 2. If the current velocity was increased to more than 14.4 cm./sec. the sand bed began to move and ripples were formed. The valves (convex upward) continued to be fixed in position until a sand ripple moved past. Each then was turned over and moved into the trough behind the ripple; it remained in the trough as the ripple slowly moved downstream.

### MOVEMENT OF SHELLS

Most of the whole hinged shells moved over the sand bed by rolling with their longest dimension perpendicular to the current; however, others slid or rolled end over end. At higher current velocities almost all of these latter shells would probably roll with their longest dimension perpendicular to the current, because this position affords the least resistance to movement. Most of the sliding shells maintained a constant orientation relative to the current, but the individuals usually had different orientations. Both sliding and rolling were episodic; a shell slid a few centimeters in a few seconds, then remained fixed for several minutes, and slid or rolled again. The episodic nature of the movement may have been due to the intermittent action of eddies which locally increased the mean velocity enough to initiate movement, but soon dissipated and no longer moved the shell.

The *Terebratulina* shells moving over an immobile sand bed came to rest at random orientations relative to the direction in which the current was moving. In a fossil state these shells would give no clue to the direction of the water movement at

TABLE 2

Movement of Brachial Valves of *Terebratulina septentrionalis*
(Initial Orientation Concave Upward)

| No. | Weight (gms.) | Behavior At Current Velocity (cm./sec.) | | | | |
|---|---|---|---|---|---|---|
| | | 8.6 | 9.4 | 10.6 | 11.6 | 14.4 |
| 18 | 0.257 | | | | Turned over | |
| 17 | 0.217 | | Slid 2 cm. | Turned over | | |
| 19 | 0.135 | | Slid 10 cm. | Turned over | | |
| 20 | 0.112 | | | Turned over | | Rolled and slid 2 cm. |
| 21 | 0.102 | Twisted 5° | Slid 20 cm. | Rolled 20 cm. end over end, concave upward | Moved out of flume | Moved out of flume |
| 22 | 0.042 | Slid several cm. | Slid 10 cm. and turned over | Slid 30 cm. | Moved out of flume | Moved out of flume |

the time they were deposited. What is more significant to paleoecology is that a small number of shells may have a chance parallel orientation, but that there may be any relation between the shell orientation and the current direction.

Single brachiopod valves moved both by sliding and by turning over so that they were alternately convex upward and downward. It was noticed that the single valves which became buried always did so in a convex-upward attitude, this position seemingly being most stable in the flume. According to the evidence of these tests, however, there is no reason to believe that orientation in sedimentary rocks can be demonstrated by the direction of convexity of a small number of valves, because a sudden stilling of the flow in the flume would have found some valves convex upward and others downward. The sequence of sedimentary rocks may be strongly suggested by consistent orientation of the direction of convexity of a considerable group of brachiopod valves (Shrock, 1948), but the possibility of error increases as the number of valves diminishes.

## SUMMARY

1. Some terebratuloid brachiopods are moved by currents in a flume which are moving no faster than natural currents found at a depth of more than 1000 fathoms in the Pacific Ocean.
2. The very low effective density of a shell and its enclosed water permit it to be moved by running water even though it weighs hundreds of times as much as any one of the motionless grains of sand over which it is rolled.
3. The velocity required to initiate the motion of a shell depends on the sphericity (shape) of the shell as well as on the size and weight. The smaller the effective density, the more important the shape.
4. Shells which are more difficult to move than the subjacent sand settle into scours which are formed in the sand around them.
5. The movement of a shell is a function of both current velocity and size of the subjacent sand grains. The same current moves a shell on one stream bed but not on another, depending upon the sand size.
6. The orientation of a small number of movable shells is essentially random in relation to current direction.

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# PLEISTOCENE CLIMATE IN NEW MEXICO

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ABSTRACT. Recently published meridional profiles of the mean temperature of the free atmosphere provide an opportunity to apply meteorologic upper air data to the problem of snowlines. The modern snowline of the Rocky Mountains is shown to be nearly identical to the mean level of the 0°C. isotherm for the summer months, corroborating the well-known postulate that snowlines are controlled by summer temperatures. This postulate is applied in speculating on the annual march of temperature in glacial time in New Mexico. The mean annual temperature so derived is applied to the hydrologic balance of a late Pleistocene lake in the closed basin of Estancia, New Mexico, in an attempt to check the computation for that lake made by Antevs.

THE line that separates areas of snow accumulation from those lower areas where snow disappears in summer is the regional snowline (Flint, 1947). The Pleistocene snowline discussed here is the approximation furnished by the level of cirque excavation.

The altitude of the snowline of Wisconsin time was approximately 12,000 feet in the southern Rocky Mountains and decreased in height northward. Data on the elevations of Wisconsin and the present snowlines have been published by Klute (1928) and Louis (1926). Depending on how much snow blows over the mountain crest, the snowline on an individual mountain range is not at the same elevation on opposite sides. This was true in Wisconsin time as well as at present and contributes to the difficulties of establishing the exact position of the Wisconsin snowline.

Certain of Klute's (1928) snowline profiles have been replotted in figure 1. His meridional profiles for the modern and Pleistocene snowlines are included in figure 1a for Japan, central Europe, Mexico, and the southern Rocky Mountains. A profile for the southern Rocky Mountains along the 110° W. Long. has also been plotted from the map of Louis (1926).

On the basis of the distribution of fossil marmots, Stearns (1942) suggests that the snowline of north central New Mexico might have been depressed 4500 feet during Wisconsin III time. He thinks that although the 2000 feet of depression suggested by Klute probably was meant to apply to the larger Wisconsin II ice advance, it is too small even for the smaller

$W_3$ advance. It will be noted from figure 1a that Stearns' suggestion agrees better with Louis' profile than does the smaller snowline depression proposed by Klute for the area.

All these profiles show a comparable magnitude of snowline depression for different parts of the world at this latitude, a resemblance which has been discussed in detail by Klute (1928).

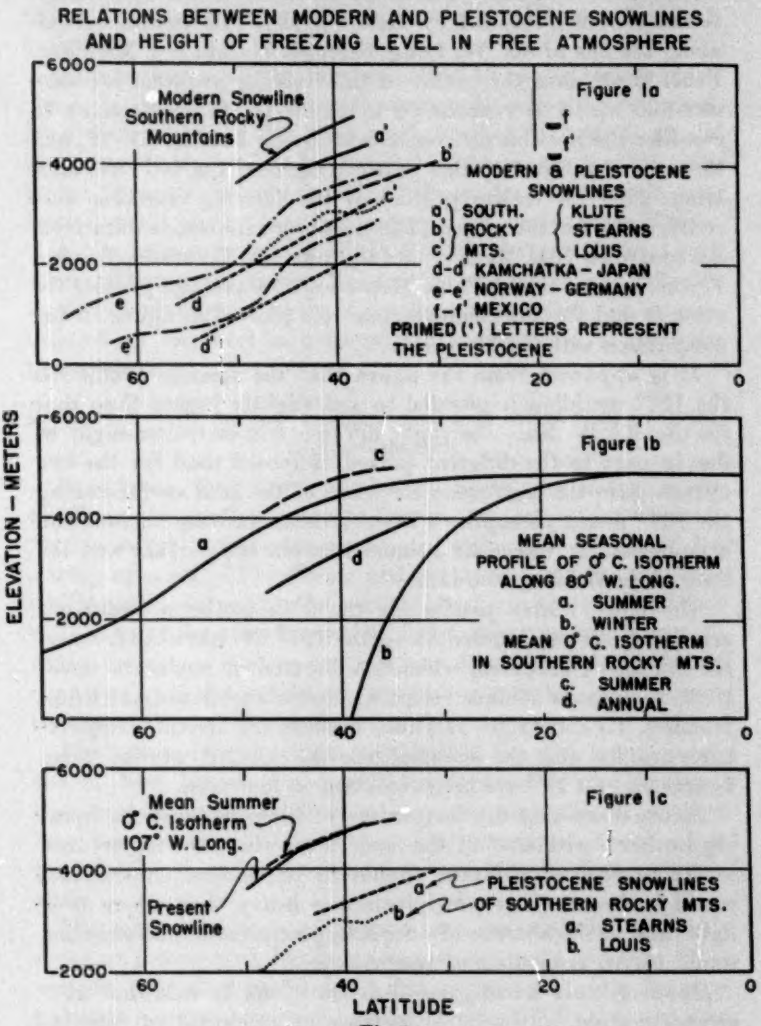



Fig. 1

### MERIDIONAL TEMPERATURE PROFILES IN THE FREE ATMOSPHERE

The modern network of upper air meteorological stations (radiosonde) provides data of direct interest to the problem of snowlines. A profile representing average upper air conditions for summer and winter from the arctic to the equator has recently been published by Hess (1948). His profile extends along the line of 80° W. Long. through Florida and Michigan. From Hess' data the profile of the freezing isotherm for summer and winter is reproduced in figure 1b. It is necessary to consider the possible difference between his data at 80° W. and the area of interest to this paper lying near the 107° W. meridian. For this reason profiles of the freezing isotherm were constructed for the period 1946-48 using radiosonde data from Albuquerque, New Mexico, Grand Junction, Colorado, Lander, Wyoming, and Great Falls, Montana. The average profiles for summer and for the complete year are plotted in figure 1b for comparison with the Hess data.

It is apparent from the figure that the summer profile for the 107° meridian is parallel to and slightly higher than that for the 80° W. line. The slight difference in elevation might be due in part to the different period of record used for the two curves. Also the high mean elevation of the land surface along the 107° meridian implies a high elevation heating surface and a consequently warm air column between the surface and the level of the freezing isotherm.

The mean winter profile for the 0°C. isotherm could not accurately be constructed along the 107° W. meridian because the stations considered, which are located at moderate elevations, have mean surface temperatures in winter near or below freezing. To clarify the relations between the free air temperature profiles and the snowline curves, selected profiles from figures 1a and 1b have been replotted in figure 1c.

Before discussing the comparison of the profiles of the freezing isotherm with that of the modern snowline, the importance of the precipitation factor should be emphasized. A snowline would be lower where precipitation is heavy than where it is light, and in the absence of adequate precipitation, no snowline would occur, regardless of temperature.

However, as a broad generalization it can be said that at a given elevation, any general increase in precipitation with in-

creased latitude in the Rocky Mountain area is small enough to be nearly obscured by large local variation resulting from different exposure, topography, and other local features.

It seems valid, therefore, to assume that the close correspondence of the profiles of freezing temperature in the free atmosphere in summer and the modern snowline, indicated by figure 1c, results from a causal relation between the two factors.

If the modern snowline were controlled by winter temperature alone, its elevation would not decrease with latitude northward from about latitude 30°, and south of that latitude it would bend sharply upward to be parallel to the winter freezing isotherm. It seems evident, then, that the modern snowline is controlled, with respect to temperatures, by summer conditions. This has been asserted by Klute (1928), Antevs (1928), and others. Their viewpoint on this matter was based primarily on studies of glaciers in which it has been shown that the magnitude of an ice sheet is predominantly controlled by summer temperature.

## ESTIMATES OF POSSIBLE TEMPERATURES IN PLEISTOCENE TIME IN NEW MEXICO

It is clear that any speculation concerning meteorologic conditions in another geologic time is subject to grave error. On the other hand, certain ideas of value can be gained by setting up a set of hypotheses and then analyzing the relations which would ensue. In the present analysis these hypotheses will, in part, be stated quantitatively. Assignment of specific values to factors such as temperature should be construed as a quantitative statement of an assumption and not as an assertion of reality.

The first assumption made here is that the Pleistocene snowline in New Mexico was controlled by summer temperature. For the moment variations in precipitation will be omitted from consideration. It is proposed to investigate the possible variations in snowline by assuming variations in temperatures alone.

The mean lapse rate of temperature (rate of decrease with elevation) measured by soundings varies only slightly from year to year at a particular point and only slightly between points in a given geographic region. Conrad (1942) has shown

that lapse rates are remarkably similar over large portions of the globe. For the approximation desired here, it will be assumed, therefore, that the lower troposphere above New Mexico had the same lapse rate in Pleistocene time as at present. This assumption would not apply near the edge of a large glacier but appears to be reasonable for an area some distance from the edge of the major ice sheets, as was New Mexico.

At levels near the freezing isotherm, the Albuquerque radiosonde data in July 1947 and 1948 showed a decrease of temperature with height amounting to about 8 Centigrade degrees per 1000 meters. This rate is somewhat higher than the average for winter at the same station, and being based on a short period of record, may be too high to represent an average summer condition. To be in accord with the data for a large number of areas studied by Conrad, a value of 6 C.° (10.8F.) per 1000 meters will be used in the analysis.

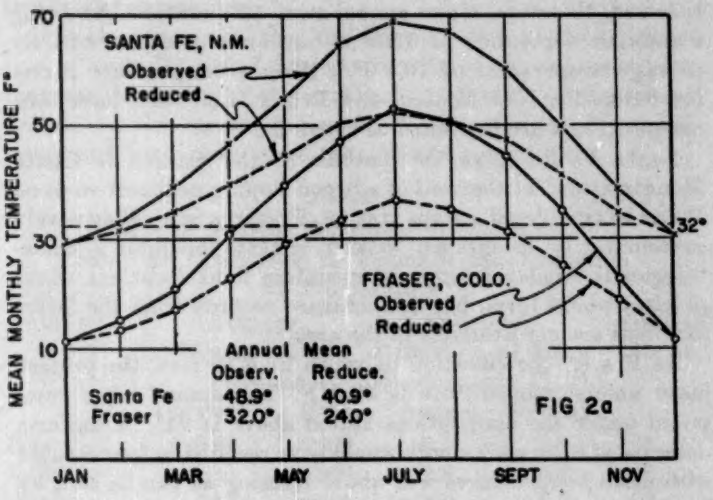
The second assumption is, then, that if the snowline were lowered 1000 meters, the July mean temperature at a given place would be decreased 6 C.° (10.8F.).

It is probable that glacial times were more different from the present in summer than in winter. A blanket of snow over Canada and northern United States provides cooling by radiation just as intense as if there were a great thickness of ice under the snow. Though the thickness of the ice has certain meteorologic effects, particularly owing to the considerable mass of air which it displaces, the main difference in winter probably lies in the permanence of the snow cover during glacial times compared with the alternation of snow cover and lack of snow which characterizes the modern winter in the latitude band from 40° to 50° N. Greater duration of cooling would make winter considerably colder over a large glacial mass and at its margin than at some distance south of the ice sheet. As far south as New Mexico, it is probable that the coldest month was little if any colder than the present. Thus it is postulated for purposes of discussion that the lowering of summer temperature was much greater than the lowering of winter temperature.

To put this postulate in quantitative terms, it will be assumed initially that in glacial times, Santa Fe, elevation 7000 feet, had the same average January temperature as at present. Later, various amounts of lowering of winter temperature will be discussed. Consideration of summer lapse rates leads to the

hypothesis that a lowering of the snowline would be accompanied by a decrease of July temperature by 10.8 F.° per 1000 meters depression. It will be assumed, further, that the mean

POSTULATED RELATIONS BETWEEN PRESENT AND PLEISTOCENE TEMPERATURES AND THE SNOWLINE



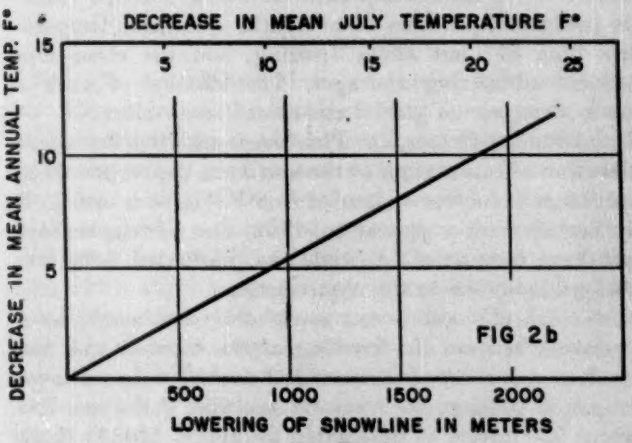




Fig. 2

temperature of each other month would be decreased by a constant percentage of the difference between the temperature of that month and January temperature. In other words, there would be a graduated reduction of the temperature of each month, with the maximum reduction in July and no reduction in January.

Such a reduction provides a new annual march of temperature and, therefore, a new annual mean temperature. Assuming a snowline depression of 1500 meters or a reduction of July average temperature of 16.2 F.°, the new temperature curves for Santa Fe, New Mexico, and Fraser, Colorado, have been computed and are presented in figure 2a.

Santa Fe lies near the foothills of the Sangre de Cristo Mountains and at the head of a broad sloping pediment surface. It can be considered a slope station. Fraser is in a valley nearly surrounded by mountains. Neither of these locations is climatologically similar to exposed mountain flank locations where glaciers would form, but temperature records from the latter locations are not available in the area.

At Fraser, the elevation of which is 8670 feet, the present mean annual temperature is 32.0°F. The annual mean computed under the assumptions stated above is 24°. A uniform decrease of 8° in each month would have resulted in four months with mean temperatures well above freezing as can be seen by inspection of figure 2a. In modern times the same four months have above freezing mean temperatures. The graduated reduction here postulated provides three months with mean temperatures less than 37° but above freezing, and the other nine months with subfreezing averages. The efficacy of such a reduction in bringing on glacial conditions seems clear.

At the latitude of Fraser, the Pleistocene snowline lay about at the elevation of this station at the maximum depression. Had the temperature reduction amounted to 8 F.° in each month, it is nearly certain that a glacial condition due to temperature would not have been attained, while the graduated reduction postulated probably meets the requirement.

Under the set of assumptions used here there would be a definite relation between the lowering of the snowline and the corresponding reduction of summer and annual temperatures. From the graph of figure 2b it can be seen that if the snowline were lowered 925 meters as postulated by Antevs (1935) there

would be a reduction of July temperature by about 10°F. and of mean annual temperature by 5 F.°. Antevs estimated the lowering of mean annual temperature to be 8 F.° on the basis of the latitudinal gradient of elevation of the modern snowline.

It can be concluded, then, that the application of the method used here gives results of the same order of magnitude as those of Antevs and extends the reasoning to define the annual distribution of temperature.

It is clear, however, that the determination of the temperature of a glacial period depends directly on the value used for the mean depression of the snowline. Application of the present method to the various estimates of the snowline depression mentioned previously gives the following results:

TABLE 1

Use of Various Estimates of Pleistocene Snowline Depression to Estimate the Reduction of Temperature

| Author | Average Depression of Snowline | | Estimated Reduction of Mean Temperature (F.°) | | Glacial Stage |
|---|---|---|---|---|---|
| | (meters) | (feet) | Annual | Summer | |
| Klute | 650 | 2000 | 3.5 | 7.0 | $W_2$ ? |
| Louis | 1800 | 5500 | 9.8 | 19.6 | ? |
| Antevs | 925 | 2800 | 5.0 | 10.0 | ? |
| Stearns | 1500 | 4500 | 8.2 | 16.4 | $W_3$ |

## LAKE ESTANCIA

In north-central New Mexico, bordered by the Sandia-Manzano Mountains on the west and Mesa Jumanos on the south, is a broad closed basin at an elevation of about 6000 feet. This flat grassy valley is at present partly covered with small farms where the raising of frijoles (pinto beans) and small herds of cattle supports a scattered population. It was early recognized by Meinzer (1911) that this basin was once the bed of a lake, which at its maximum extent was 150 feet deep and had a surface area of 450 square miles. Bryan and McCann (unpublished) have discussed in detail the origin of the basin and present evidence which indicates that there were actually two lake stages, of which the second was smaller and contained within the one outlined by Meinzer.

Small glaciers existed in Wisconsin time in the highest parts of the Sangre de Cristo range 100 miles north of the Estancia Valley. The peaks of these mountains exceed 12,000 feet in elevation, but because of their relatively low latitude, the largest glacier located above the present site of Santa Fe, was only 7 miles long. Melt waters from these glaciers fed either the Rio Grande to the west or the Pecos River system to the east, but did not contribute water to the closed basin of Lake Estancia.

The time relations between Lake Estancia and the glacial chronology have been studied by Antevs (1935, 1949) in an attempt to date the artifacts and bones found on the Llano Estacado. It is one purpose of the present discussion to review the Antevs analysis.

*Hydrologic Balance of Lake Estancia.*—Having made estimates of the relation between changes in temperature and the corresponding amounts of depression of the snowline in Pleistocene time, it is possible to examine the relation of these temperature changes to the water supply of Lake Estancia. The plan will be as follows. Given the depression of the snowline as determined from geologic evidence, the corresponding temperature changes will be used to estimate the change in annual evaporation. The resulting value of evaporation will be applied to Lake Estancia at its maximum stage to determine whether the lake could have existed under conditions having the same precipitation as that now experienced in the locality. If the lake could not be maintained under the assumed conditions of reduced evaporation, then it must be postulated that a greater rainfall existed at that time than at present, and some estimate of the magnitude of this increase might be made.

Values of evaporation from open lakes in the western United States are meagre. Although there are a reasonable number of evaporation data for Class A pans, a coefficient must be chosen to convert even roughly the pan data into evaporation from the free water surfaces of lakes.

Though there is no direct relation between air temperature and evaporation, a plot of mean monthly temperature against the mean evaporation in respective months is a graph widely used in hydrologic practice. The graph shows a hysteresis loop proceeding through the seasons. Figure 3a shows these loops for a number of lakes in the Great Basin determined by measurement of inflow and outflow (Harding, 1945). As might

be expected, evaporation generally increases with mean air temperature.

It is necessary to estimate such a hysteresis loop for central New Mexico. No evaporation record is available for Estancia. The nearest record is a Class A evaporation pan at Santa Fe which has been plotted as the full line in figure 3b. The rainfall and temperature conditions at Santa Fe are nearly identical to those of the Estancia Valley. Though the topography is somewhat different, Estancia being more exposed and for this reason possibly more windy, the Santa Fe curve will be applied after adjustment. Using a coefficient of .70 to reduce the pan observations to conditions of a free water surface, the evaporation measured for each month at Santa Fe was reduced

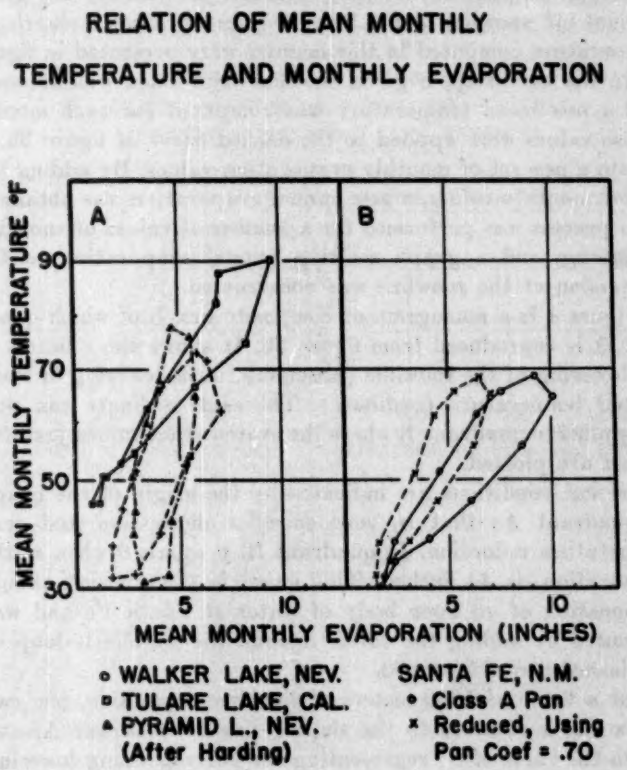



Fig. 3

to provide the hysteresis loop plotted as the dashed line in figure 3b.

Using the method outlined, the annual evaporation from a lake surface at Santa Fe is estimated to be 44 inches. Interpolating from the map of Furness (1947) a value of 48 inches would be obtained. His map of reservoir evaporation was derived from pan records similarly adjusted by a coefficient of .70. The map also indicates that Estancia at present would experience an annual evaporation about 3 inches greater than Santa Fe. Since this is much smaller than other possible errors in the present analysis, the Santa Fe record will be assumed applicable to Estancia.

A quantitative method has been specified for computing a new mean temperature for each month of the year for any given amount of snowline depression. Curves of annual march of temperature computed in this manner were presented in figure 2. In the next step, a given snowline depression was assumed and a new mean temperature was computed for each month. These values were applied to the dashed curve of figure 3b to obtain a new set of monthly evaporation values. By adding the twelve monthly values, a new annual evaporation was obtained. This process was performed for a number of values of snowline depression and a graph relating annual evaporation to the depression of the snowline was constructed.

Figure 4 is a nomogram or composite graph of which quadrant A is reproduced from figure 2b. It shows the relation of the lowering of the snowline (abscissa) to the lowering of mean annual temperature (ordinate). The same ordinate can now be applied to quadrant B where the evaporation values just discussed are plotted.

Present conditions are indicated by the origin of the graph in quadrant A; that is, zero snowline depression and zero temperature reduction. In quadrant B, $y$ equals 0 when $x$, the evaporation, is 44 inches. This value is the present annual evaporation of an open body of water at Santa Fe and was computed by adding the values around the hysteresis loop of the dashed line of figure 3b.

For a value of 1500 meters of snowline depression, one can follow the arrows up to the sloping line of quadrant A, and left to the value of 8° representing the corresponding lowering of mean annual temperature. Proceeding horizontally from

$y = 8°$ to the evaporation line and thence downward, one can read the value of 29 inches for the annual evaporation corresponding to a snowline depression of 1500 meters.

Let us return for a moment to the assumption that in Pleistocene time the mean January temperature remained equal to that of the present time while the summer temperature was considerably lower. Though winter might have been somewhat colder than the present, for the reasons already stated it is probable that the reduction in winter was small compared with that of summer. To test the effect of a reduced winter temperature, assume that the mean January temperature was 5F.° lower than at present and that the July temperature was reduced 16.2F.° in accordance with a snowline depression of 1500 meters. Under this set of assumptions the mean annual temperature would be lowered 11.8F.°. It can be seen that the new

COMPOSITE GRAPH OF POSTULATED
RELATIONS BETWEEN HYDROLOGIC FACTORS
AFFECTING PLEISTOCENE LAKE ESTANCIA

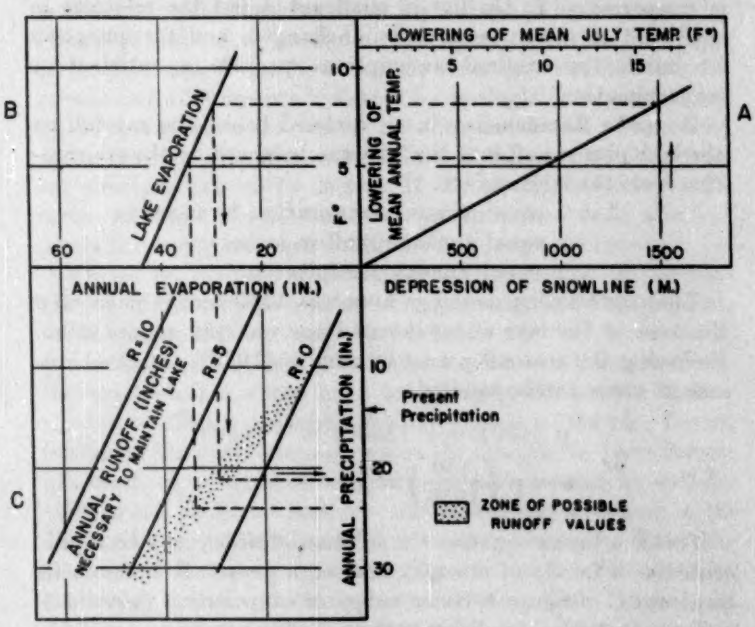



Fig. 4

assumption of a specific lowering of January temperature would increase the slope of the curve shown in quadrant A of figure 4.

Using the new annual march curve of temperature a new value of annual evaporation can be obtained. The assumptions and results are summarized below:

Assume:

1) Depression of snowline of 1500 meters
   Therefore: July temperature lowered 16.2F.°
2) January temperature lowered 5F.° and intervening months proportionately

Compute from above assumptions:

1) Annual mean temperature reduction of 11.8° F.
2) Annual evaporation from lake, 26 inches

As would be expected, the additional assumption of a lower winter temperature would reduce the mean annual temperature. The consequent reduction of evaporation would be relatively small because the evaporation occurs primarily in summer. In summary, an assumed reduction of winter temperature provides a steeper slope to the line in quadrant A but the relations in quadrant B remain essentially unchanged, and for purposes at hand, the original assumptions provide a satisfactory approximation.

As Lake Estancia lay in an enclosed basin, the rainfall on the lake plus runoff into the lake was balanced by the evaporation from the lake surface.

Let e equal annual evaporation in inches
r equal annual runoff in inches
p equal annual precipitation

The contributing drainage area was 1550 square miles, and the area of the lake at maximum stage was 450 square miles. Following the reasoning used by Antevs (1935), the total volume of water can be equated:

$$p\,(450) + r\,(1550) = e\,(450)$$

or

$$e - p\left(\frac{450}{1550}\right) = r$$

This is a linear equation the solution of which may be represented as a family of straight lines on a graph. It is shown in quadrant C of figure 4. Given values of evaporation (abscissa) and precipitation (ordinate), the runoff $r$ necessary to main-

tain the lake can be read off the graph by interpolation between the sloping lines.

It is obvious that for any given value of annual precipitation only a certain range of annual runoff values can occur in nature. A map of annual runoff for the United States has been published by Langbein (1949). It shows values of .25 inches near Estancia, .50 inches near Santa Fe, and an increase of values with elevation in central New Mexico. The relation of rainfall to runoff existing under present vegetative types and the geologic formations occurring in New Mexico determines the possible range of values, and this range is indicated by the stippled area in quadrant C of figure 4.

It is now possible to determine the rainfall necessary to maintain Lake Estancia under various assumed conditions of evaporation which in turn are determined by temperature. Referring back to the example cited above, a depression of the snowline of 1500 meters, one can follow the arrows along the dashed line into quadrant C and observe that according to the assumptions made, a precipitation of 21 inches would be necessary to maintain the lake at its high stage. The reasoning so far has considered no change of precipitation but only changes of temperature. It can be reasoned, then, that the snowline depression of 1500 meters indicated by geologic data and caused by temperature alone would not be associated with a low enough evaporation to maintain Lake Estancia under the present precipitation of 14 inches. If the precipitation were 21 inches at that time, the increased precipitation would also apply in the mountains and would in itself lower the snowline.

Therefore, the case of no temperature reduction will be considered. If the temperature were the same as that of the present, the lake evaporation would be 44 inches ($y = 0$, $x = 44$, in quadrant B). To maintain Lake Estancia under that condition, the precipitation would have to be about 30 inches. Such a rainfall would have brought the upper part of the pine forest, bordering the spruce zone, down to the margins of Lake Estancia. Such an occurrence would surely be indicated by well-developed soil profiles, which are not to be found anywhere in the Estancia area. Actually, some streams tributary to Lake Estancia have not discharged enough water since the lake receded to breach the lake shore deposits damming them (Bryan and McCann, manuscript). It is impossible to believe, then, that

increased precipitation without lowered temperature could account for the lake.

Great variations in rainfall would change the vegetative associations sufficiently to affect the runoff coefficient. Also the change in the period of snow cover might have an important effect on runoff. However, as long as the postulated changes require only moderate changes in precipitation and do not require major changes in the vegetation in the Estancia Valley, the use of modern rainfall-runoff relation in the present analysis seems justified.

The analysis leads to the conclusion, therefore, that Lake Estancia must have existed at a time when temperature was lower and precipitation higher than the present. How much did each of these factors contribute to the lowering of the snowline? A postulation of the relation of temperature, explored in some detail in the present study, has been made possible owing to two basic facts: first, the modern snowline seems controlled to a considerable degree by summer temperature, and second, tht average lapse rate of temperature is so nearly uniform around the earth in the middle latitudes that an assumption of similar lapse rate in Pleistocene time seems very reasonable.

The relation of snowline to precipitation is much more difficult to postulate because it has not been investigated in detail in the Rocky Mountains even for modern conditions. Although a reasonable guess might be made, it would be founded on an even less logical set of assumptions than the temperature relation already discussed.

Consider the graphs of figure 4 for an assumed depression of the snowline of 1000 meters. Following the dashed line around the graph from that value, it is seen that a precipitation of 24 inches is necessary for maintaining the lake. That the difference between 24 inches and present 14 inches would account for the extra 500 meters of snowline depression necessary to make the 1500 meters inferred from geologic evidence, is a speculation which cannot be supported or tested.

It seems desirable to mention one other feature of the present analysis. Antevs (1935) used very similar reasoning to that presented here and concluded that Lake Estancia could not have existed at the same time that glaciers occurred in the mountains. He postulated (Antevs, 1949) that the lake postdated the maximum glaciation and existed 10,000 to 12,000

years ago at a time when both temperature and precipitation were higher than the present. He chose values of 20 inches for precipitation and 35 inches for evaporation as likely during the existence of the lake. These values require a runoff of about 4.5 inches from a precipitation of 20 inches, a high runoff coefficient for the western country. Assuming, however, that this might still be possible, his postulation of a temperature higher than that of the present would necessitate an increase in evaporation. The evaporation data from Santa Fe used in the present study indicate that 35 inches of evaporation would require a lower, not a higher temperature. Antevs used the evaporation of Lake Tahoe, California, as a criterion. The question is whether the Lake Tahoe evaporation provides a better measure of evaporation in New Mexico than an adjusted Santa Fe record.

The present analysis supports the conclusion of Antevs that Lake Estancia must have existed in a period more humid than the present. Antevs interpreted the necessity for increased precipitation as an indication of a post-glacial date, while the present study leads to the conclusion that a decreased temperature should also be necessary, indicating contemporaneity of the lake with glaciers in the mountains. These opposing viewpoints point to the hazard of using a date assigned to the lake as a measure of the age of associated artifacts.

The writer gratefully acknowledges the help of Prof. Kirk Bryan, Prof. Chas. F. Brooks, and Dr. V. Conrad, of Harvard University, and Mr. G. E. Harbeck of the U. S. Geological Survey, who read the manuscript and made many valuable suggestions.

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# COMMUNICATIONS

## LYELL, GREEN, HILGARD, AND THE MISSISSIPPI VALLEY LOESS

Sir Charles Lyell published the tenth edition of his *Principles of Geology* at London in 1867. The first edition had been published in 1830-32. On Sept. 25, 1866, Sir Charles had written to Col. James Green of Dayton, Ohio, the holograph letter quoted below. This letter, with the original envelope and its postage stamp, are pasted in the front of the first of the two volumes of the tenth edition of Lyell's *Principles* which now belong to the present writer.

"Dear Sir," Sir Charles wrote to Colonel Green from 53 Harley Street, London, "I have just received your letter informing me of the very interesting discovery of the remains of the buffalo fish in the loess. Although the chapter in which I shall be able to allude to it, is in the hands of the printer it will not be too late to get in a reference to it. I am glad you are pursuing your researches in that direction. It will throw great light on the former geological history of the Valley of the Mississippi—As my proofs are coming in fast & I am keeping up an active correspondence, you will oblige me much by letting Professor Hilgard of Oxford Mississippi know that I have received his valuable letter a few days ago. I am sorry that he did not know that my book has taken a longer time to get through the press than I had anticipated as I should like very much to have learnt from Mr. Conrad whether the only two species from the Artesian well of New Orleans which he (Mr Hilgard) had been unable to identify were known as living shells or not. They were I think a Cardium & Tellina. I fully expect that they will turn out to be recent species because the *Gnathodon cuneatus* & several other living shells are found at a much greater depth Even if they should not be known shells they might be living in the Gulf for we have found *Muresc Vaginatus* which I have figured in Chap XIII of the last edition of my Elements in the Mediterranean. It is now excessively rare but was evidently abundant towards the close of the Newer Pliocene Period.

"But I must not indulge in this subject at present but hope to write to Mr Hilgard at some later day & in the mean time I beg to thank him for his prompitude in sending me the latest information which he had obtained.

"I am, dear Sir

"very truly yours

"Cha Lyell"

Colonel Green added an asterisk after the word "obtained" in Sir Charles Lyell's final paragraph, and then wrote on the opposite page, below Lyell's signature, the following note.

"P.S. It was Prof Hilgard who urged me to forward immediately to Sir Charles Lyell, a Description of the fossil remains that I discovered in the Loess of the Mississippi Near Vicksburg so that It might be published in the New addition of his 'Principles of Geology'."

"James Green"

Upon a number of pages of my copy of the 1867 edition of Lyell's *Principles of Geology* there are interesting pencilled annotations by Colonel Green, for example on page 464 of Vol. I where the buffalo fish in the loess near Vicksburg are described by Lyell. It may not be without interest to observe that the 1867 copy of Lyell's *Principles* which contains the holograph letter quoted above is also annotated with the words "Col. James Green with the compliments of Wm. M. Smith purchased in London. Aug. 1868." One wonders whether still other evidences of early correspondence between American geologists and European geologists are extant. For Lyell letters to Rev. Charles Kingsley and to Rev. Charles Pye Smith, both Englishmen, see Henry P. Zuidema, Jour. Geology, vol. 55, no. 5, Sept., 1947, pp. 439-445.

LAWRENCE MARTIN
WASHINGTON, D. C.

## ENROLLMENT OF GEOLOGISTS AND GEOPHYSICISTS IN THE NATIONAL SCIENTIFIC REGISTER

Planning for the mobilization and effective use of the scientists and engineers of the United States for purposes of national defense is now under way. Appointment of a committee composed of leaders in science and industry by the National Security Resources Board is a recent step. The representative of the geological professions on this committee is E. De Golyer; the chairman is Charles A. Thomas, vice-president of Monsanto Chemical Co. and former president of the American Chemical Society.

A basic element in the entire program for maximum use of the nation's scientific manpower will be an adequate scientific register. This will tell us the magnitude and nature of the national pool of technological competence.

In order to secure this information, the N.S.R.B. was instrumental last summer in causing the establishment of a National Scientific Register Office in the U. S. Office of Education. This office has let contracts with the American Chemical Society, the National Research Council and the American Institute of Physics for enrollment of all physical and biological scientists and mathematicians. Enrollment will be accomplished through the societies and the register will also be kept up to date through the societies. The American Geological Institute has been asked to ensure the enrollment of all geologists and geophysicists.

The project must start essentially from scratch because the records of the World War II National roster are completely out of date. Also, with the tremendous increase in the number of working scientists since 1945, its records are very incomplete.

Some geologists and geophysicists who are included in American Men of Science, filled out a comprehensive registration form in 1948. These men *will not* be asked to answer all the questions on the new simpler form, but will be asked to fill out basic questions in the interest of uniformity.

The following methodology is being established for this project to ensure effective coverage. It is hoped that use of this method will spread the work, prevent wasteful and annoying duplication, and get the job done more promptly and effectively.

The register will include all geologists and geophysicists with a bachelor's degree (or equivalent) and all graduate students.

Circularization will be accomplished by district committees. These will center in active local societies, state geological surveys and major departments.

The register will be used for the following purposes—

(a) by Scientific Advisory Committees in the Selective Service

System. It is expected that these committees will review appeals for deferment which are made to The President and that the information on file with the Register will be used in the consideration of such cases.

(b) by the National Security Resources Board. This agency is charged with responsibility for the planning of general mobilization both military and civilian, and will use the information in determining the requirements for scientific manpower in various activities.

(c) by the National Research Council and by the American Geological Institute in determining the distribution and availability of earth scientists among the various specialized occupations.

(d) as a means whereby Government agencies may identify personnel with specialized training or experience for unusual work requirements.

(e) in the preparation of studies and recommendations to Government agencies, such as the National Security Resources Board, concerning the needs for geological scientists in civilian occupations.

In addition, it will furnish information concerning the composition and structure of the geological professions which will be invaluable.

The full cooperation of every member of the geological professions is earnestly requested so that our part in this national effort may be performed quickly and effectively.

# REVIEWS

*Elementary Pile Theory*; by H. Soodak, and E. C. Campbell. Pp. ix, 78. New York, 1950 (John Wiley & Sons, Inc., $2.50).—This booklet is noteworthy in two important respects. First, it opens to physicists at large a field still somewhat shrouded in mystery, but naturally interesting to students who are alive to modern research. And it may be said, to the credit of the authors, that their treatment will doubtless attract readers by its clarity, directness and simplicity. Secondly, the little volume revives a part of classical physics that is frequently neglected in the training of physicists during these times of formalized pursuits. For it presents in palatable fashion the elements of the kinetic theory, bringing out the visual beauty of its concepts without the dry appeal to transport equations, distributions in phase space and the like. The contents of the book, if injected discriminately into a standard course in the kinetic theory, would enliven it greatly.

Using fairly simple mathematics (i.e. nothing beyond calculus) the authors treat the essential details of the functioning of chain-reacting piles. Illustrations are used freely in explanation of the physical and mathematical ideas encountered. The style is precise and non-discursive, but the economy of statement is not carried to the extreme which often discourages readers of technical treatises. Still, if the book has any fault at all, it might lie in its confinement to issues directly related to the pile, in its failure at times to point to other situations in which similar reasoning is applicable. But the brevity of the text makes this restriction unavoidable.

HENRY MARGENAU

*Stratigraphy and Paleontology of the Brownsport Formation (Silurian) of Western Tennessee*; by Thomas W. Amsden. Peabody Museum of Natural History, Yale University, Bulletin 5. Pp. 138; 30 figs., 34 plates. New Haven, 1949 (Yale University Press, $5.00).—The Brownsport formation has long been a center of paleontologic interest as a collecting ground for fine Silurian fossils. Since the pioneer work of Troost, many geologists have added to our knowledge of Brownsport rocks and fossils, notably Roemer, Safford, Foerste, Pate and Bassler, and Springer. Amsden's report presents the results of a detailed stratigraphic and paleontologic study. An outstanding contribution is the careful description and illustration of 97 species of brachiopods, corals, cystoids, and blastoids, of which 37 species and one genus are new. Except for Springer's work on the crinoids, the Brownsport fauna has never been systematically studied, so that with the publication of Amsden's report a description of this rich and varied fauna is available for the first time. With this as a basis, Amsden documents the correlation of the Brownsport formation with the Bainbridge limestone

of Missouri, the Louisville limestone of Kentucky, the Henryhouse shale of Oklahoma, and part of the Niagaran dolomites in the Chicago area.

In its stratigraphic conclusions this report differs from the interpretation first made by Pate and Bassler in 1908, and later endorsed by other workers, that the Brownsport is to be considered a group comprising in ascending order the "Beech River formation," "Bob limestone," and "Lobelville formation." A summary statement of the Brownsport published as part of a larger work by C. W. Wilson, Jr. in 1949 follows this interpretation. Amsden believes that the basis of this subdivison is invalid. Whereas the "Bob" has been considered as a sheet of massive limestone separating the thin-bedded, argillaceous limestones and shales of the "Beech River" and "Lobelville" formations, Amsden's work indicates that the "Bob" comprises rather local and lenticular facies equivalents of "Beech River" and "Lobelville" lithology. This interpretation of the stratigraphy, based on detailed examination and measurement of 53 sections, together with a biostratigraphic analysis indicating that Bassler's formations are not faunally distinct, prompts Amsden to abandon the tripartite division. JOHN IMBRIE

*The Geology, Paragenesis, and Reserves of the Ores of Lead and Zinc*; Report of the 18th Session of the International Geological Congress, part 7, Great Britain, 1948; K. C. DUNHAM, Editor. Pp. 400, 99 figs. London, 1950.—The International Geological Congress has made another valuable contribution to economic geology in compiling a wealth of information on the geology, paragenesis and reserves of the ores of lead and zinc.

The urgent need for such a report is well pointed out by the opening remarks of the chairman, Professor W. R. Jones: "Half of the world's supply of lead and zinc is produced in North America . . . It is over a quarter of a century since the last discovery of a lead and zinc deposit of major importance . . . Only a few of the major fields contain proved reserves sufficient at their present rate of production to last twenty years or so . . . Production during the last twenty-five years has been greater than during all previous mining history . . . Here, then, is a challenge to the geologists and mining engineers of the world to find more deposits and to increase production." The object of the symposium is to "help the geologists meet this challenge by increasing our knowledge concerning the geological conditions most suitable for the occurrence of the different types of these ores."

Lead and zinc deposits "have been formed in the earth's crust at levels varying from some of the deepest which can be observed up to the top of the permanent groundwaters." A fivefold classifica-

tion is given—hypothermal in regional-metamorphic environments; pyrometasomatic-mesothermal; deep mesothermal veins and replacements; leptothermal veins and replacements; telethermal replacements and disseminations. Hypothermal deposits contain the largest reserves.

A very comprehensive table has been prepared of the principal lead and zinc mines of the world, their country rock, associated igneous rocks, mineral paragenesis, nature of ore shoots, reserves, assays of ore and current production. Although the production and reserve figures are subject to the limitations imposed by a deficiency of information, the table is a valuable summary of the world's literature.

The report is presented in place of the usual volume on world resources, as prepared for other sessions. However, it follows the pattern of the earlier reports in presenting well-written descriptions of individual lead and zinc deposits. Each description is written by authors well qualified for the task, and includes an abstract in English and a bibliography.

Most countries which hold important positions as lead and zinc producers have contributed papers. Russia is a notable exception. Forty-four authors have contributed 33 papers which may be divided as follows: 2 from Canada, 7 from the United States, 2 from Mexico, 1 from Peru, 2 from Australia, 1 each from Tanganyika, Nigeria, Morocco and Tunisia, 2 from Portugal, 4 from Italy, 1 each from Jugoslavia, Greece and Poland, 2 from Germany, 1 from Great Britain, 2 from Sweden and 1 from China. Papers on newly described districts are presented, including the Taxco Mining District, Mexico, and deposits in French Morocco, Tunisia and Tanganyika. New information on the Mississippi Valley, Franklin Furnace, Bisbee and others bring our storehouse of knowledge up to date. An excellent description of the Cerro de Pasco properties is presented. The Kupferschiefer is described and a supergene origin reaffirmed. Several authors suggest that supergene leaching of lead has taken place. A tendency to retain theories of supergene deposition of sulfides is shown by the statement of one author " . . . no igneous rocks of whatever kind can be found. The ore consists chiefly of galena in which silver content is usually high. Gangue minerals are calcite and quartz. This type of deposit represents, probably, the product of groundwater concentration of non-igneous origin." Theories on sedimentary lead and zinc deposits seem to be restricted to Europe.

The publication represents an international exchange of facts and theories which will work to the benefit of all geology, and especially those geologists directly concerned with lead and zinc.

CHARLES H. SMITH

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